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# CCLIV.—*A Modified Dichromate Method for the Estimation of Glycerol. The Hydration of Curd Fibres of Sodium Palmitate.*

By HAROLD BENSON BENNETT.

THAT curd fibres of soap contain bound water, whether chemically combined or sorbed,* has been shown (J., 1919, **115**, 1300; 1921, **119**, 1369, 1669) by negative sorption of sodium hydroxide and by indirect analysis using sodium sulphate and glycerol as reference substances. This result was confirmed by the vapour-pressure method (J., 1921, **119**, 1374) for fibres of sodium palmitate formed in presence of saturated solution of sodium chloride at 90° which have the composition $NaP,2{\cdot}1H_2O$. However, only a few isolated values have been established.

The great difficulty is that all the reference substances hitherto investigated are themselves more or less sorbed by the soap. Only in the presence of a very great excess of another salt is the sorption of a given salt minimised, but even so, probably it is not entirely eliminated. Thus from its very nature the method of negative sorption yields only minimum values for hydration.

Glycerol is the only non-electrolyte which is not sorbed in presence of saturated sodium chloride solution. The present communication shows that negative sorption of glycerol occurs even in the complete absence of salt and that the hydration of curd fibres of sodium palmitate at room temperature is greater than that represented by $NaP,10H_2O$.

## EXPERIMENTAL.

The clear solution obtained by heating and shaking known quantities of sodium palmitate and glycerol solution in a stoppered glass bottle was allowed to curd in a thermostat at the desired temperature. The mother-liquor (lye) was extracted by suction through a filter plate in an Alihn funnel, the air supply being freed from carbon dioxide. The funnel was immersed in a small thermostat, while the lye was allowed to drip into a vacuum flask at room temperature. Froth was condensed by slightly heating the flask.

The weights of glycerol, sodium hydroxide, and sodium palmitate in the mother-liquor were determined and subtracted from the total weight to give the weight of water. The hydration of the curd is $\frac{1000}{18{\cdot}02 \times N_s}\left(1 - \frac{N_w}{N_{w'}}\right)$ mols. $H_2O$ to 1NaP, where $N_s$ is the weight

* The decision will probably have to be left to *X*-ray examination (compare Piper and Grindley, *Proc. Roy. Soc.*, 1923, **35**, 269).

normality of curd and $N_w$ and $N_{w'}$ are the original and final weight normalities of glycerol.

*Estimation of Glycerol.*—The acetin method, requiring 1·25 to 1·50 gms. of glycerol, was inapplicable to this work, in which not more than 0·2 to 0·5 gm. in dilute solution was available. Since pure sodium palmitate was used, it was possible to modify the Hehner dichromate method (*J. Soc. Chem. Ind.*, 1898, **17**, 330), estimating excess of dichromate by titration with sodium thiosulphate after addition of potassium iodide. The following procedure must be followed to obtain results accurate to 0·1 per cent.

To the clear solution obtained by warming 10 gms. * of lye with 28 c.c. of water, free from carbon dioxide, 50 c.c. of sulphuric acid (water diluted to twice its volume with concentrated sulphuric acid †) were added and the mixture allowed to cool to complete the precipitation of the palmitic acid.‡ A quantity of potassium dichromate (dried at 115°) about 0·1 gm. in excess of that required to oxidise the glycerol, was added, and washed down with water free from carbon dioxide. The mixture was heated under an air condenser by boiling water for exactly 2 hours, quickly cooled, and immediately made up to a litre with distilled water. To 50 c.c. samples of the resulting solution, crystals of potassium iodide were added and about 2 c.c. of 50 per cent. sulphuric acid. After 5 minutes, the solution was diluted to 600 c.c. and the end-point obtained by titration with $0{\cdot}01N_v$-sodium thiosulphate and starch, a Sheringham daylight lamp being used. Different samples gave results agreeing within a few hundredths of 1 per cent.

The slight correction for the dichromate lost through oxidation of the superficial layer of liquid palmitic acid was determined by blank analyses of known soap solutions both with and without glycerol and was found to be reproducible to a few milligrams. It is more than proportional to the excess of dichromate. Thus for 10 gms. of solution containing 0·07 gm. of sodium palmitate and 5 per cent. of glycerol, treated as described but with varying excesses of dichromate amounting to 0·1, 1·0, 2·0, and 3·7 gms., respectively, the correction was 8, 23, 33, and 122 mgs. respectively, corresponding to errors in the glycerol determination of 0·22, 0·63, 0·89, and 3·26 per cent. of the total glycerol present (taken as 100 per cent.).

* For other weights all the following quantities are altered in the same proportion.

† Referred to subsequently as 50% sulphuric acid. Its density is well above the minimum density, 1·230, found to be necessary by Kellner (*Z. deut. Oel-Fett. Ind.*, 1921, **14**, 751).

‡ Serious error results if the dichromate is added before the soap has been decomposed by sulphuric acid.

It is evident that where the excess of dichromate used is not more than 0·1 gm. the correction can be accurately estimated and applied. This correction is not affected by appreciable variations in the amount of palmitate or even of water present.

To determine free alkali, a solution of at least 5 gms. of lye in about four times the weight of recently boiled alcohol, which had been tinted very faintly pink by alkali and phenolphthalein, was titrated back to the original colour. The two constituents of sodium palmitate were estimated by adding an excess of standard hydrochloric acid, filtering, and titrating the filtrate and the residue, the latter in 60 to 80 per cent. alcohol, recently boiled. In the estimation of very dilute soap lyes there was often a wide discrepancy between these two results; nevertheless the mean was taken.

Concentrations of curds and glycerol are expressed in weight normality, $N_w$ (mols. per 1000 gms. of water), and the others in volume normality, $N_v$ (equivalents per litre).

*Results.*

Preliminary experiments with a different method of glycerol analysis showed that $0{\cdot}5N_w$ curds of sodium palmitate, a fortnight old, at 25° in presence of $0{\cdot}6N_w$ glycerol were hydrated at least to the extent represented by $NaP,8H_2O$. The first experiment by the modified dichromate method gave a value as high as $NaP,15H_2O$. The results necessarily depend on small differences between large numbers and an error of 1 per cent. in the estimation of glycerol corresponds to an error of 0·6, 1·1, and 2·2 mols. of hydrate water for 1·0, 0·5, and $0{\cdot}25N_w$ curds, respectively.

The final results are collected in Table I. The first curd in the table was $3\frac{1}{2}$ months old, all the others were between 4 and 6 days old. On the whole, taking the preliminary results also into account, the hydration seemed to increase with age. The curd certainly appears and feels much drier after it has been kept in a closed vessel; compare the great diminution of solubility found by Laing and McBain (J., 1920, **117**, 1506). The specimen of Kahlbaum's sodium palmitate used had the empirical composition $NaP,0{\cdot}5H_2O$ and therefore 0·5 has been added to each of the results in the last column of Table I.

The data are sufficient to prove that sorption of glycerol by curd fibres is almost or quite negligible even in the absence of salt. The hydration of $1{\cdot}0N_w$ curds of sodium palmitate is constant at $NaP,4{\cdot}3H_2O$, whereas that of $0{\cdot}25N_w$ curds exceeds $NaP,10H_2O$. This divergence is inexplicable, since the results are reproducible. We expected that the curd fibres separating from the more concentrated solution (and at higher temperature) would be the less

TABLE I.

*Hydration of Curds of Pure Sodium Palmitate in presence of* $0{\cdot}6N_w$ *Glycerol at* 17° *to* 25°.

| Curd. | 10 Gms. of lye contained | | | | $N_w$ Glycerol. | | Hydration, |
|---|---|---|---|---|---|---|---|
| $N_w$. | $C_3H_8O_3$. | NaP. | NaOH. | $H_2O$. | Before. | After. | $NaP,xH_2O$ |
| 0·2496 | 0·5146 | 0·0316 | 0·0027 | 9·4511 | 0·5626 | 0·5916 | 11·4 |
| 0·2483 | 0·5139 | 0·0360 | (0·0005) | 9·4496 | 0·5645 | 0·5907 | 10·4 |
| 1·000 | 0·5163 | 0·0874 | 0·0047 | 9·3916 | 0·5626 | 0·5984 | 3·8 |
| 1·000 | 0·5280 | 0·0874 | 0·0047 | 9·3899 | 0·5626 | 0·5991 | 3·9 |
| 1·000 | 0·5270 | 0·0690 | 0·0049 | 9·3991 | 0·5626 | 0·6089 | 4·7 |
| 1·000 | 0·5249 | 0·0690 | 0·0049 | 9·4012 | 0·5626 | 0·6064 | 4·5 |
| 1·000 | 0·5234 | 0·0874 | 0·0047 | 9·3845 | 0·5645 | 0·6057 | 4·3 |

hydrated, but not to the extent found. There are no other measurements extant with which to compare these results. A suggested explanation is given below.

The data of column three constitute a measurement of the solubility of the curd fibres. It will be seen that the curd fibres produced from $1{\cdot}0N_w$ solution are far more soluble than those from $0{\cdot}25N_w$ solution, a result which Laing (*loc. cit.*) had previously substantiated for sodium oleate. The solubility here found also agrees with that observed by Laing and McBain, hence there seems to be a real difference between the curd fibres separating from different concentrations of soap solution. The difference may be due to the fact, since ascertained by Langdon, that a $1{\cdot}0N_w$ solution of sodium palmitate is isotropic only above 79°. In preparing normal soap curds the sodium palmitate is first brought completely into solution by heating, and the solution must pass, at least partly, into the condition of a transparent, plastic, anisotropic liquid (Lehman's liquid crystal; Friedel's liquide à conique *) before any curd fibres appear, since they commence to separate only below 67°. On the other hand, the $0{\cdot}5N_w$- and $0{\cdot}25N_w$-solutions of sodium palmitate are ordinary isotropic solutions throughout the whole range of temperature and, as we have here found, the curd fibres have at least twice the hydration of those formed from $1{\cdot}0N_w$ solution.

*Summary.*

Glycerol is negatively sorbed by curd fibres of sodium palmitate at room temperature even in the absence of any salt. The curd fibres separating from $1{\cdot}0N_w$-solution (which is anisotropic, liquid crystal, liquide à conique) have the approximate composition $NaP,4{\cdot}3H_2O$ and appear to be several times more soluble than those from (ordinary isotropic) $0{\cdot}25N_w$-solution, namely, $NaP,10H_2O$. A modification of the dichromate method for estimating glycerol

* Compare McBain, *Nature*, 1924, **113**, 534.

has been devised which is much more accurate than the original and, with slight alteration, is of general applicability.

My thanks are due to Prof. McBain for suggesting this work and to the Research Fund Committee of the Colston Research Society of the University of Bristol for grants for materials.

UNIVERSITY OF BRISTOL. [*Received, April 16th*, 1924.]

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## CCLV.—*The Velocity of Benzylation of certain Amines.*

By DAVID HENRY PEACOCK.

A CONSIDERABLE amount of work has been done on the velocity of formation of quaternary ammonium salts (compare Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589, etc.; Thomas, J., 1913, **104**, 594; Cox, J., 1921, **119**, 142; Hawkins, *J.*, 1922, **121**, 1170). The velocity of reaction between primary or secondary bases and halogen compounds has not been examined to the same extent. Cox (*loc. cit.*) studied the rate of reaction between bromoacetophenone and aniline and Menschutkin (*Z. physikal. Chem.*, 1900, **34**, 157) studied the rates of reaction between certain aromatic amines and allyl bromide and methyl bromide.

Benzylated amines are usually prepared technically by the action of benzyl chloride on the appropriate amine and an account is now given of some of the results obtained, as these are of interest also in connexion with the process of activation. If in a bimolecular reaction each molecular species becomes independently activated, then the energy of activation will be the sum of the energies of activation of each species. If, on the other hand, one substance has a polarising or activating effect on the other, the energy of activation will be specific for each reaction (and possibly for each medium). This effect will also be apparent in the results obtained by altering the concentration of each reactant independently.

Other assumptions may be made as to the mechanism of the reaction, but in this paper attention is particularly directed to the assumption of independent energy increments. The total energy increment for the reaction between benzyl chloride and aniline can be calculated, with the help of the usual equation, from the temperature coefficient of the reaction velocity. In a similar way, the energy increments for the reactions between benzyl chloride and *p*-toluidine, *p*-nitrobenzyl chloride and aniline, and *p*-nitrobenzyl chloride and *p*-toluidine have been determined. We then have :—

$E_1 = E_A + E_B$; $E_2 = E_A + E_C$; $E_3 = E_D + E_B$; $E_4 = E_D + E_C$.

Therefore $E_1 - E_2 = E_3 - E_4$.

The energy increments thus found were :—aniline and benzyl chloride, 13,454 cals.; aniline and *p*-nitrobenzyl chloride, 14,678 cals.; *p*-toluidine and benzyl chloride, 16,050 cals.; and *p*-toluidine and *p*-nitrobenzyl chloride, 11,860 cals.

From the first set of figures the difference between the energy of activation of *p*-nitrobenzyl chloride and benzyl chloride is 1224 cals., and from the second set, — 4190 cals. The hypothesis of independent activation energies does not hold in this case. The energy of activation of any particular molecular species in a bimolecular reaction would then appear to depend on the nature of the other molecule with which it is to react.

In the reaction under consideration there is the possibility that the amine and halogen compound form a loose complex, which then, possibly under the influence of another molecule of amine, rearranges itself, giving ionic chlorine. The velocity coefficient indeed tended to increase with increasing concentration, and this effect depended mainly on the amine concentration.

The action of benzyl chloride upon aniline can be represented by the equations :—

(1) $NH_2Ph + CH_2PhCl \rightarrow NHPh{\cdot}CH_2Ph,HCl.$
(2) $NHPh{\cdot}CH_2Ph,HCl + NH_2Ph \rightarrow NH_2Ph,HCl + NHPh{\cdot}CH_2Ph.$
(3) $NHPh{\cdot}CH_2Ph + CH_2PhCl \rightarrow NPh(CH_2Ph)_2,HCl.$ Etc.

The velocity of the first reaction would be represented by the expression $dx/dt = k(a - x)(b - x)$ as used by Menschutkin (*loc. cit.*), but if we take into account the action of the aniline upon the hydrochloride formed, then the velocity becomes $dx/dt = k(a - 2x)(b - x)$. There is no doubt that dibenzylaniline is formed; it was isolated in many experiments and can easily be prepared by the benzylation of benzylaniline at quite low temperatures.

Both the original Menschutkin velocity equation and the amended form give similar results for the reaction velocity during the initial stages, but for the later stages the Menschutkin equation usually gives more constant values of $k$. In view of the undoubted formation of dibenzylaniline this can only be ascribed to compensating errors; the Menschutkin equation neglects the fall in concentration of aniline due to combination with hydrochloric acid and also the effect of dibenzylation.

## Experimental.

The benzyl chloride and aniline were fractionally distilled before use and boiled within 0·2°. The *p*-nitrobenzyl chloride and *p*-toluidine were crystallised from petroleum. "Absolute"

alcohol (99·6%) was used as solvent; it was not further dried, as the experiments were carried out during the rains. The flasks, pipettes, and burettes were all standardised for these experiments. In carrying out a series of determinations, a solution of benzyl chloride in alcohol was made up of such a strength that a particular 5 c.c. pipette delivered 2·5 gms. (0·02 mol.); an aniline solution also was made up so that 0·08 mol. could be delivered from a 10 c.c. pipette; *p*-toluidine and *p*-nitrobenzyl chloride were weighed. The benzyl chloride (0·02 mol.), alcohol, and aniline (0·08 mol.), all at the temperature of the thermostat, were well mixed, the volume was made up to 50 c.c., 5 c.c. were withdrawn and added to 20—25 c.c. of solvent naphtha and ice-cold water and shaken. After separation, the solvent naphtha was washed with water and the aqueous extracts were washed with solvent naphtha. Pure precipitated chalk was then added to the aqueous solution, which was boiled, filtered, and titrated with *N*/10-silver nitrate with potassium chromate as indicator. In the case of less volatile bases which were not removed by distillation in steam on boiling the solution, the aqueous layer was made alkaline with pure sodium carbonate and extracted with solvent naphtha and then acidified with a slight excess of nitric acid and treated as before. Some of the experimental details are given below :—

TABLE I.

Velocity of reaction between aniline and benzyl chloride. Conc. of aniline 1·6 mols. per litre (*b*), and of benzyl chloride 0·4 mol. per litre (*a*). 5 C.c. samples were titrated with 0·972 *N*/10-silver nitrate.

Temperature 35°.

| Time. | C.c. of $AgNO_3$. | $a - x$. | $b - x$. | $k$ (Menschutkin) $\times 10^5$. | $k$ (amended) $\times 10^5$. |
|---|---|---|---|---|---|
| 0 | 0·35 | 0·3931 | 1·593 | | |
| 30 | 3·4 | 0·333 | 1·533 | 152 | 156 |
| 60 | 5·97 | 0·2832 | 1·4832 | 154 | 161 |
| 120 | 9·62 | 0·2118 | 1·4118 | 150 | 162 |
| 150 | 11·08 | 0·1832 | 1·3832 | 150 | 165 |
| 210 | 13·39 | 0·1380 | 1·3380 | 150 | 170 |

Temperature 45°.

| | | | | | |
|---|---|---|---|---|---|
| 0 | 0·70 | 0·3864 | 1·5864 | | |
| 15 | 3·71 | 0·3272 | 1·5272 | 309 | 318 |
| 30 | 6·00 | 0·2824 | 1·4824 | 296 | 310 |
| 45 | 8·08 | 0·2416 | 1·4416 | 300 | 320 |
| 60 | 9·55 | 0·2128 | 1·4128 | 290 | 314 |
| 90 | 12·39 | 0·1570 | 1·3570 | 290 | 335 |
| 120 | 14·37 | 0·1182 | 1·3182 | 301 | 347 |
| 180 | 16·80 | 0·0706 | 1·2706 | 297 | 358 |

The values of $k$ (Menschutkin) were calculated from the equation $dx/dt = k(a - x)(b - x)$,

$$\text{whence } k = \frac{1}{t_2 - t_1} \cdot \frac{1}{b - a} \log. \frac{b - x_2}{a - x_2} \cdot \frac{a - x_1}{b - x_1}.$$

The concentrations were expressed in gram-molecules per litre and logarithms to the base 10 were used.

The values of $k$(amended) were derived from the equation $dx/dt = k(a - x)(b - 2x)$,

$$\text{whence } k = \frac{1}{t_2 - t_1} \cdot \frac{1}{2(b/2 - a)} \log. \frac{b/2 - x_2}{a - x_2} \cdot \frac{a - x_1}{b/2 - x_1}.$$

$t$ was measured from the first reading, not from the time of mixing.

The following are the mean values of $k$ (amended) for the initial periods of the reactions studied; in each case the concentration of the amine was 1·6 $M$ and of the benzyl chloride 0·4 $M$.

TABLE II.

Velocity coefficients at 35° and 45°.

| Reaction. | $k_{35°}$. | $k_{45°}$. |
|---|---|---|
| Aniline–benzyl chloride ..... | 0·00157 | 0·00315 |
| Aniline–*p*-nitrobenzyl chloride ..... | 0·000588 | 0·00125 |
| *p*-Toluidine–benzyl chloride ..... | 0·00217 | 0·00495 |
| *p*-Toluidine–*p*-nitrobenzyl chloride ... | 0·00137 | 0·00252 |

*p*-Nitrobenzyl chloride reacts much more slowly than benzyl chloride; this was to be expected from the residual valency effect of the nitro-group; Olivier (*Rec. trav. chim.*, 1922, **41**, 646) found a similar effect in the hydrolysis of benzyl chloride and *p*-nitrobenzyl chloride. The hypothesis of alternating polarities explains this effect equally well.

From the above values of the velocity coefficients the energy of activation, $E$, of each reaction is calculated from the equation $\log. k_1/k_2 = E/R(1/T_2 - 1/T_1)$; the values are given earlier.

When the concentrations of the aniline and benzyl chloride were changed, the value of the velocity coefficient also changed.

TABLE III.

Velocity coefficients at 35° at various concentrations.

| | | | |
|---|---|---|---|
| Aniline ..... | 1·6$M$ | 0·8$M$ | 1·6$M$ |
| Benzyl chloride ..... | 0·4$M$ | 0·2$M$ | 0·2$M$ |
| $k$ ..... | 0·00157 | 0·00122 | 0·00148 |

It would appear that the variation of the concentration of the aniline has the major effect and this suggests that the aniline exerts a catalytic action, possibly by forming a loose, reactive complex or

by means of an induced polarisation. Further work is being done on this point and also on the variation in the velocity of reaction with different bases. The following preliminary and approximate values have been obtained for the velocity coefficients ($k$) of the reactions, in alcohol at 40°, between benzyl chloride and the bases named ($c$ and $c'$ = conc. of the base and benzyl chloride, respectively).

TABLE IV.

Velocity coefficients at 40°.

| Base. | $c$. | $c'$. | $k \times 10^5$ | Base. | $c$. | $c'$. | $k \times 10^5$. |
|---|---|---|---|---|---|---|---|
| Aniline ..... | 4 | 2 | 354 | *p*-Chloroaniline ..... | 2·0 | 0·5 | 232 |
| ,, ..... | 2 | 1 | 300 | 2 : 5-Dichloroaniline... | 4 | 1 | 17 |
| ,, ..... | 4 | 1 | 383 | Monomethylaniline | 4 | 1 | 562 |
| *o*-Toluidine ..... | 4 | 1 | 70 | Monoethylaniline | 4 | 1 | 202 |
| *p*-Toluidine..... | 4 | 1 | 660 | Monobenzylaniline | 2 | 1 | 120 |
| *o*-Chloroaniline ..... | 4 | 1 | 44 | | | | |

Concentrations are given in gram-mols. per litre and logarithms to the base 10 were used.

The benzyl derivatives were isolated and those which were secondary bases were converted into the benzoyl (A) and the *p*-toluenesulphonyl (B) derivatives.

| | Base. | A. M. p. | B. | | Base. | A. M. p. | B. |
|---|---|---|---|---|---|---|---|
| Benzyl-*o*-chloroaniline ... | 44° | 111° | — | Benzylaniline | — | 105° | 133° |
| Benzyl-*p*-chloroaniline ... | 45 | 138 | — | Benzyl-*o*-toluidine | — | 65 | — |
| Benzyl-2 : 5-dichloroaniline | 47 | 69 | — | Benzyl-*p*-toluidine | — | 127 | 126 |

Further work is in progress on the rate of interaction between (1) primary and secondary amines and halogenobenzenes in which the halogen is attached to the nucleus, and (2) primary amines and halogenated anthraquinone compounds. It has already been observed that methylaniline reacts with *o*-chloronitrobenzene at a very much slower rate than does aniline, whereas with benzyl chloride the reaction velocity is faster with methylaniline. In the case of halogenated anthraquinone compounds the catalytic action of copper salts is well known; with benzyl chloride and aniline at 40°, no such catalytic action was observed. Still more interesting was the observation that the velocity coefficient fell off considerably towards the end of the reaction between 4-bromo-1-methylaminoanthraquinone and *p*-toluidine. No signs of a similar falling off were observed with benzyl chloride and *p*-toluidine. 2 : 4-Dibromo-1-aminoanthraquinone showed this decrease in velocity coefficient to a much smaller extent than did 4-bromo-1-methylaminoanthraquinone, so that the decrease seems connected with the 2-position in the latter compound and is possibly another case of the well-known

tendency of the 4-halogen in anthraquinone compounds to migrate to the 2-position, where it is less reactive.

In conclusion, I wish to thank the British Dyestuffs Corporation (Huddersfield) for supplying many of the materials used in this work.

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## CCLVI.—*Diazonium Tetrachloroiodides and Plumbichlorides.*

By FREDERICK DANIEL CHATTAWAY, FRANK LESLIE GARTON, and GEORGE DAVID PARKES.

ALTHOUGH the trihalides have long been known (Griess, *Annalen*, 1866, **137**, 50; Hantzsch, *Ber.*, 1895, **28**, 2754), diazonium perhalides of a higher order appear not to have been obtained hitherto. The diazonium tetrachloroiodides now to be described are among the most easily made and most stable of diazonium derivatives. They separate quantitatively when cooled solutions of diazonium chlorides are poured into a cooled solution of iodine trichloride in strong hydrochloric acid. They are all yellow, crystalline substances which dissolve sparingly in, and can be recrystallised from, a dilute solution of iodine trichloride in strong hydrochloric acid. From this solvent they separate in very small, bright yellow prisms. They are extraordinarily stable and many can be preserved indefinitely with little change if sealed up in glass tubes, or kept in a desiccator filled with chlorine. They generally melt sharply, although always with decomposition and occasionally with explosion.

These compounds appear to have a constitution resembling that of the recently described tetrachloroiodides of organic bases (Chattaway and Garton, this vol., p. 183) and should probably be represented by co-ordination formulæ similar to those usually assigned to diazonium chloroaurates, *e.g.*,

$$Ph{\cdot}N_2\begin{bmatrix} Cl & Cl \\ & I \\ Cl & Cl \end{bmatrix} \qquad Ph{\cdot}N_2\begin{bmatrix} Cl & Cl \\ & Au \\ Cl & Cl \end{bmatrix}.$$

The chemical behaviour of the diazonium tetrachloroiodides is in the main similar to that of the simple diazonium salts such as the chlorides, but occasional differences are met with owing to the presence of so large a proportion of halogen.

When they are added to a solution of hydrogen iodide or to an

acidified solution of potassium iodide, the corresponding iodobenzene derivative is produced, with a quantitative liberation of iodine:

$$Ar{\cdot}N_2{\cdot}ICl_4 + 4HI = ArI + N_2 + 2I_2 + 4HCl.$$

This reaction in presence of acetic acid affords an easy method of analysing the compounds by titration of the liberated iodine with standard sodium thiosulphate.

When the diazonium tetrachloroiodides are warmed with cuprous chloride or bromide, in strong acid solution, or with potassium cuprous cyanide, the diazo-group for the most part is replaced by chlorine, bromine, or cyanogen, but a small quantity of the corresponding iodo-compound is also formed.

When heated with water, the diazo-group is replaced by hydroxyl, phenols being produced. These are to some extent substituted by the excess of halogen, and various chlorophenolic compounds are formed as by-products.

When added to excess of strong aqueous ammonia, the diazonium tetrachloroiodides yield azides together with nitrogen iodide.

When heated with alcohol, they behave differently from the diazonium chlorides, the diazo-group being mainly replaced by chlorine and only to a subordinate extent by hydrogen.

Diazonium chlorides also form a series of remarkably stable compounds with lead tetrachloride.*

Diazonium plumbichlorides are so sparingly soluble that they separate almost quantitatively when solutions of diazonium salts are added to a solution of lead tetrachloride in strong hydrochloric acid. They appear to have a constitution resembling that of the chloroplatinates and should probably be represented by similar co-ordination formulæ, *e.g.*,

$$(ArN_2)_2\begin{bmatrix} Cl & & Cl \\ Cl & Pb & Cl \\ Cl & & Cl \end{bmatrix} \qquad (ArN_2)_2\begin{bmatrix} Cl & & Cl \\ Cl & Pt & Cl \\ Cl & & Cl \end{bmatrix}.$$

The diazonium plumbichlorides are all crystalline solids, yellow in colour, although varying slightly in shade. They are very stable when dry, specimens left in corked tubes showing no signs of decomposition after some weeks.

On heating, they decompose explosively at definite temperatures which vary only slightly with the rate of heating. They cannot be recrystallised even from hydrochloric acid saturated with chlorine.

All the diazonium plumbichlorides react quantitatively with

* When this work had been completed, a paper on the same subject appeared (Sakellarios, *Ber.*, 1923, **56**, 2536) in which several of these compounds are described. In the present paper a number not there mentioned are described, the explosion temperatures only of the others being added.

potassium iodide in the presence of acids. As with the diazonium tetrachloroiodides, this reaction affords an easy method of analysing these compounds. Iodine is liberated quantitatively and the diazo-group is replaced by iodine.

When diazonium plumbichlorides are added to solutions of cuprous chloride in strong hydrochloric acid or of cuprous potassium cyanide, nitrogen is evolved and chloro- or cyanogen derivatives are formed.

They are immediately decomposed by water, lead dioxide and the corresponding phenol being formed. The phenol is acted upon to some extent by the excess of halogen present, and mixtures of chlorinated phenols are produced. When added to dilute sulphuric acid, chlorination of the phenol first formed occurs to a much greater degree, whilst lead sulphate is precipitated quantitatively.

Ammonia reacts readily with the diazonium plumbichlorides, yielding the azides almost quantitatively.

As with the diazonium tetrachloroiodides, the diazonium plumbichlorides, when boiled with alcohol, yield chloro-derivatives, the diazo-group being mainly replaced, not by hydrogen, but by chlorine. Aldehyde is formed by the action of excess of chlorine on the alcohol (Chattaway and Backeberg, this vol., p. 1098), whilst the lead separates as lead chloride.

The diazonium plumbichlorides react very similarly to the tetrachloroiodides and to the diazonium chlorides, and in consequence of their great stability seem likely to prove of considerable use.

## Experimental.

### *Diazonium Tetrachloroiodides.*

*Benzenediazonium Tetrachloroiodide*, $C_6H_5 \cdot N_2 \cdot ICl_4$.—A solution of benzenediazonium chloride (aniline 5 gms., conc. hydrochloric acid 75 c.c., water 20 c.c.; only a slight excess of sodium nitrite) was added slowly to a cooled solution of tetrachloroiodic acid ($HICl_4$), made by passing chlorine into a suspension of 15 gms. of powdered iodine in 80 c.c. of strong hydrochloric acid until all the iodine had been converted into the trichloride, as shown by the disappearance of the brown colour of the iodine monochloride first formed. Pure benzenediazonium tetrachloroiodide separated as a bright yellow, microcrystalline powder. A slow stream of chlorine was passed through the mixture for an hour, the tetrachloroiodide was filtered off, washed with strong hydrochloric acid, and then with a little chlorine water, and finally dried over calcium chloride and a lump of lime, in a desiccator filled with chlorine.

*Benzenediazonium tetrachloroiodide* thus obtained is a bright

yellow, crystalline powder, m. p. 88° (decomp.) (Found : Cl = 37·86. $C_6H_5N_2Cl_4I$ requires Cl = 37·94 per cent.).

The following *diazonium tetrachloroiodides* were prepared by a similar method. They are all yellow, crystalline powders which, when rapidly heated, decompose at the temperatures stated : o-*toluene-*, m. p. 81·5° (Found : Cl = 36·47. $C_7H_7N_2Cl_4I$ requires Cl = 36·57 per cent.); p-*toluene-*, m. p. 95° (Found : Cl = 36·37 per cent.); o-*chlorobenzene-*, m. p. 148° [Found : Cl (added) = 34·45. $C_6H_4N_2Cl_5I$ requires Cl (added) = 34·74 per cent.]; p-*chlorobenzene-*, m. p. 111° [Found : Cl (added) = 34·94 per cent.]; 2 : 4-*dichlorobenzene-*, decomp. about 150° with liberation of iodine trichloride [Found : Cl (added) = 31·9. $C_6H_3N_2Cl_6I$ requires Cl (added) = 32·04 per cent.]; 2 : 5-*dichlorobenzene-*, m. p. 141° [Found : Cl (added) = 32·20 per cent.]; 2 : 4-*dibromobenzene-*, decomp. about 120° with evolution of iodine trichloride [Found : Cl (added) = 26·55. $C_6H_3N_2Cl_4Br_2I$ requires Cl (added) = 26·68 per cent.]; 2 : 4 : 6-*tribromobenzene-*, m. p. 135° [Found : Cl (added) = 23·00. $C_6H_2N_2Cl_4Br_3I$ requires Cl (added) = 23·23 per cent.]; o-*nitrobenzene-*, m. p. 125·5° (Found : Cl = 33·61. $C_6H_4O_2N_3Cl_4I$ requires Cl = 33·87 per cent.); m-*nitrobenzene-*, m. p. 92° (Found : Cl = 33·69 per cent.); p-*nitrobenzene-*, m. p. 103° (Found : Cl = 33·8 per cent.).

*Transformations of the Diazonium Tetrachloroiodides.*—(a) *By hydriodic acid.* Five gms. of benzenediazonium tetrachloroiodide, or of the *o*-toluene or *p*-chlorobenzene compound, were added to 15 gms. of potassium iodide in 30 c.c. of water. On acidification with acetic acid, iodine separated at once and nitrogen was evolved. The iodine was removed by the addition of a strong solution of sodium sulphite, and the whole was steam-distilled, when iodobenzene, b. p. 189°, *o*-iodotoluene, b. p. 204°, and *p*-chloroiodobenzene, m. p. 56°, respectively, were obtained in quantitative or almost quantitative yield.

(b) *By cuprous cyanide.* Ten gms. of 2 : 4 : 6-tribromobenzenediazonium tetrachloroiodide were added little by little to excess of a hot solution of potassium cuprous cyanide. Copious evolution of nitrogen occurred and a solid containing some cuprous iodide separated. This was separated, and extracted repeatedly with hot alcohol. On cooling the alcoholic solution a mixture of 2 : 4 : 6-tribromobenzonitrile, m. p. 127°, and 2 : 4 : 6-tribromo-1-iodobenzene, m. p. 105·5°, was obtained. These were separated by fractional crystallisation from alcohol. By using sufficient of this solvent the nitrile crystallised out practically pure, a mixture of 2 : 4 : 6-tribromo-1-iodobenzene with a little nitrile remaining in the mother-liquor. This was evaporated, and the process repeated

until finally a solution was obtained from which 2 : 4 : 6-tribromo-1-iodobenzene separated in a pure condition.

(c) *By water.* *o*-Nitrobenzenediazonium tetrachloroiodide was heated with water until evolution of nitrogen had ceased, sodium sulphite was added, and the product steam-distilled, the distillate being collected in small fractions of 20 to 30 c.c. The earlier fractions contained almost pure *o*-nitrophenol (m. p. 45°); the last fractions yielded a similar amount of 4-chloro-2-nitrophenol (m. p. 87°); whilst the middle fractions consisted of a mixture of the two. This reaction is analogous to that which takes place when benzenediazonium nitrate is decomposed with water, when nitrophenols appear as the main products.

(d) *By cuprous chloride.* Ten gms. of *p*-nitrobenzenediazonium tetrachloroiodide were added gradually to a warm solution of cuprous chloride in concentrated hydrochloric acid. Much nitrogen was almost immediately evolved together with a little iodine. The latter was removed by adding a little sodium sulphite. The pale yellow solid remaining, which consisted of *p*-chloronitrobenzene mixed with cuprous iodide, was extracted with hot alcohol, from which, on cooling, *p*-chloronitrobenzene separated in colourless plates, m. p. 83° (yield 70 per cent.) (compare Griess, *J. pr. Chem.*, 1866, **97**, 457).

*Diphenyl*-4 : 4′-*bisdiazonium Octachlorodi-iodide.*—A diazotised solution of benzidine (base 5 gms.; concentrated hydrochloric acid 75 c.c.) was added as before to tetrachloroiodic acid (from 15 gms. of iodine and 80 c.c. of conc. hydrochloric acid). *Diphenyl*-4 : 4′-*bisdiazonium octachlorodi-iodide* separated immediately as a yellowish-brown, crystalline solid, which was washed and dried in the same way as the compounds already described. It decomposed explosively at 135—140°, the exact temperature depending on the rate of heating (Found : Cl = 37·87. $C_{12}H_8N_4Cl_8I_2$ requires Cl = 38·05 per cent.).

Diphenyl-4 : 4′-bisazoimide (Griess, J., 1867, **20**, 94) was prepared (yield about 80 per cent.) by decomposing the octachlorodi-iodide with ammonia (*d* 0·880) and ice and destroying the liberated nitrogen iodide with sodium sulphite. The diphenyl-4 : 4′-bisazoimide recrystallised from benzene, separated in glittering, pale brown spangles, m. p. 131°, decomp. 165—170°. It explodes when suddenly heated or when touched with a drop of strong sulphuric acid. If a few crystals be dropped into sulphuric acid they dissolve without explosion, forming a bright red solution.

### *Diazonium Plumbichlorides.*

Diazonium plumbichlorides are best prepared by the following general method.

The diazotised solution prepared by passing nitrous fumes into a suspension of the appropriate aniline in concentrated hydrochloric acid (5 parts) is added to an excess of a solution of lead tetrachloride obtained by passing dry chlorine into a suspension of freshly-precipitated lead dichloride in excess of concentrated hydrochloric acid until all the lead chloride has dissolved, the temperature being kept below 0°. The diazonium plumbichloride separates immediately as a yellow, microcrystalline powder. This is filtered off, and washed, first with hydrochloric acid saturated with chlorine, then with chloroform saturated with chlorine, and is finally dried for 3 days over calcium chloride and a few lumps of lime in a desiccator filled with chlorine.

The following *diazonium plumbichlorides* were thus prepared. The temperature at which the substance explodes when heated slowly is given; when placed in a bath at this temperature and heated slowly, it decomposes at a temperature (given in brackets) 1° or 2° higher: o-*toluene*-, decomp. 78° (80°) (Found: Cl = 10·61. $C_{14}H_{14}N_4Cl_6Pb$ requires Cl = 10·78 per cent.); 2 : 4-*dichlorobenzene*-, decomp. 183° (184°) [Found: Cl (added) = 9·32. $C_{12}H_6N_4Cl_{10}Pb$ requires Cl (added) = 9·24 per cent.); p-*bromobenzene*-, decomp. 139° (141°) [Found: Cl (added) = 9·26. $C_{12}H_8N_4Cl_6Br_2Pb$ requires Cl (added) = 9·00 per cent.]; 2 : 4-*dibromobenzene*-, decomp. 117° (118°) [Found: Cl (added) = 7·61. $C_{12}H_6N_4Cl_6Br_4Pb$ requires Cl (added) = 7·50 per cent.]; 2 : 4 : 6-*tribromobenzene*-, decomp. 114° (116°) [Found: Cl (added) = 6·21. $C_{12}H_4N_4Cl_6Br_6Pb$ requires Cl (added) = 6·40 per cent.]; o-*nitrobenzene*-, decomp. 120° (122°) (Found: Cl = 9·73. $C_{12}H_8O_4N_6Cl_6Pb$ requires Cl = 9·85 per cent.).

*Transformations of the Diazonium Plumbichlorides.*—Except the phenomena due to the presence of iodine, these were similar to the transformations of the tetrachloroiodides. Thus, by reaction with cuprous chloride, 2 : 4-dichlorobenzenediazonium plumbichloride gave 1 : 2 : 4-trichlorobenzene, separated by steam distillation, in 70 per cent. yield; b. p. 213°, m. p. 16° (compare Beilstein and Kurbatov, *Annalen*, 1878, **192**, 238); *p*-bromobenzenediazonium plumbichloride, reacting with excess of aqueous potassium iodide, acidified with acetic acid, gave iodine quantitatively and *p*-bromoiodobenzene, m. p. 92° (compare Griess, *loc. cit.*), in 90 per cent. yield; and 2 : 4-dibromobenzenediazonium plumbichloride and excess of hot potassium cuprous cyanide solution gave 2 : 4-dibromobenzonitrile, m. p. 81° (compare Claus and Weil, *Annalen*, 1892, **269**, 222).

When boiled with alcohol, 2 : 4 : 6-tribromobenzenediazonium plumbichloride yielded 1-chloro-2 : 4 : 6-tribromobenzene and very

little 1 : 3 : 5-tribromobenzene. Five gms. of the substance were warmed with 25 c.c. of alcohol until no further evolution of nitrogen occurred. The product was steam distilled; from the solid remaining, hot alcohol extracted 1-chloro-2 : 4 : 6-tribromobenzene, colourless needles, m. p. 87° (compare Wegscheider, *Monatsh.*, 1897, **18**, 217), in 70 per cent. yield.

Five gms. of *o*-nitrobenzenediazonium plumbichloride were heated with sulphuric acid diluted with three times its volume of water. A strong phenolic smell was noticed, but nothing was isolated by steam distillation. From the residual liquid ether removed a yellowish-brown, viscous substance which could not be crystallised, but which readily dissolved in aqueous sodium hydroxide, with a reddish-yellow colour. Taking into consideration the well-known difficulty in crystallising chlorophenols, this behaviour indicates that the product consisted of a mixture of chlorinated *o*-nitrophenols.

*Diphenyl-4 : 4′-bisdiazonium plumbichloride* separated as an orange-yellow, crystalline powder, the crystals being larger than those of any of the plumbichlorides described above. It exploded with great violence at 131°, the explosion of a small quantity in a melting-point tube being sufficient to shatter a beaker containing oil in which it was being heated (Found : Cl = 11·46. $C_{12}H_8N_4Cl_6Pb$ requires Cl = 11·46 per cent.).

When boiled with water, diphenyl-4 : 4′-bisdiazonium plumbichloride gives a good yield (66 per cent.) of 4 : 4′-dihydroxydiphenyl, m. p. 272°, with only a small quantity of a chlorinated derivative.

The following plumbichlorides have been described by Sakellarios (*loc. cit.*); only their explosion temperatures, which he does not record, are therefore given here. Benzenediazonium plumbichloride, 80—81°; *p*-chlorobenzenediazonium plumbichloride, 145—150°; *p*-toluenediazonium plumbichloride, 72—75°; *m*-nitrobezenediazonium plumbichloride, 161—163°; *p*-nitrobenzenediazonium plumbichloride, 132—133°.

### *Interaction of Diazonium Tetrachloroiodides and Plumbichlorides with Ammonia.*

It has already been noted that aromatic azoimides are formed when diazonium tetrachloroiodides and diazonium plumbichlorides are added to strong ammonia. The yields of azoimides are almost quantitative and as both the tetrachloroiodides and plumbichlorides are easily made and can as a rule be preserved in the dry state for a long time without material change these reactions form a convenient method of preparing these compounds.

Two structural formulæ have been assigned by different chemists to the aryl azoimides :

$$Ar{\cdot}N\!<\!\begin{matrix}N\\ \|\\ N\end{matrix} \quad \text{and} \quad Ar{\cdot}N{:}N{:}N.$$

The cyclic formula, however, is generally accepted, as, whatever constitution is assigned to the diazonium perhalides, it is difficult to see how their interaction with ammonia could give rise to compounds having the latter constitution.

The diazonium tetrachloroiodides so closely resemble the tetrachloroiodides of simple nitrogen bases (compare Chattaway and Garton, this vol., p. 183) that it is highly probable that they are similarly constituted, that is, that they are true diazonium perhalides. The reaction, therefore, between them and ammonia cannot be regarded as a simple elimination of halogen acid, but must involve the oxidation of a triazan ring, $R{\cdot}N\!<\!\begin{matrix}NH\\ |\\ NH\end{matrix}$, the formation of which is the first stage of the reaction. This oxidation must be effected by the hypohalogen acid produced by the interaction of ammonium hydroxide with the hydrogen tetrachloroiodide or perbromide eliminated in the formation of the ring, and subsequent hydrolysis. The reaction may be formulated thus :

$$Ar{\cdot}\underset{\|\\ N}{N}{\cdot}ICl_4 \xrightarrow{NH_4OH} Ar{\cdot}\underset{\|\\ N}{N}{\cdot}OH \xrightarrow{NH_3} Ar{\cdot}\underset{|\\ HN{\cdot}NH_2}{N}{\cdot}OH \longrightarrow$$

$$Ar{\cdot}N\!<\!\begin{matrix}NH\\ |\\ NH\end{matrix} \xrightarrow{HOCl} Ar{\cdot}N\!<\!\begin{matrix}NCl\\ |\\ NH\end{matrix} \xrightarrow{NH_3} Ar{\cdot}N\!<\!\begin{matrix}N\\ \|\\ N\end{matrix}.$$

The interaction of diazonium tetrachloroiodides with ammonia is on the whole the most convenient and least disagreeable method of preparing aryl azoimides, and several hitherto undescribed substituted aryl azoimides have been prepared in this way and their reactions studied.

2 : 4-*Dichlorophenylazoimide*.—To a paste of 2 : 4-dichlorobenzenediazonium tetrachloroiodide (20 gms.) and crushed ice, excess of strong aqueous ammonia was added (*d* 0·880), when a black solid separated, containing nitrogen iodide. The latter was removed by shaking with strong aqueous sodium sulphite, and the residual 2 : 4-dichlorophenylazoimide steam-distilled from a weak solution of sodium sulphite. The pale yellow, waxy solid which separated from the distillate crystallised from acetone or benzene in fine, long, pale yellow prisms, m. p. 54° (compare Ponzio, *Gazzetta*, 1916, **46**, ii, 56, who prepared it in poor yield by the action of hydroxylamine on 2 : 4-dichlorobenzenediazonium chloride).

When heated slowly above its m. p., it decomposes quietly at

about 160°, but if rapidly heated or sharply struck, it explodes evolving clouds of black smoke (Found : Cl = 37·95. $C_6H_3N_3Cl_2$ requires Cl = 37·73 per cent.).

The following were prepared similarly : 2 : 5-*dichlorophenylazoimide*, pale yellow, crystalline solid, m. p. 30°, very readily soluble in organic solvents, separating as an oil which only resolidifies after complete removal of the solvent (Found : Cl = 37·28 per cent.); 2 : 4-dibromophenylazoimide, pale yellow needles, m. p. 62°, from acetone or benzene (compare Griess, *J. pr. Chem.*, 1866, **97**, 454, who prepared it from 2 : 4-dibromobenzenediazonium perbromide); o-*tolylazoimide*, pale yellow oil which does not solidify even on cooling to − 10°. It boils at 70°/20 mm., but explodes when heated under atmospheric pressure.

Aryl azoimides frequently react with the greatest readiness with compounds containing double, and (still more easily) with those containing triple bonds to give triazoles, *e.g.*,

$$Ar{\cdot}N_3 + CX{:}CY \longrightarrow \begin{matrix} N{=}{=}N \\ | \\ CX{:}CY \end{matrix}\!\!>NAr$$

(compare Dimroth, *Ber.*, 1910, **43**, 2222).

Substituted phenylazoimides have been found to react in a similar manner.

1-(2 : 4-*Dichlorophenyl*)-1 : 2 : 3-*triazole*.—Acetone (20 gms.), saturated at 0° with dry acetylene, and 2 : 4-dichlorophenylazoimide (2 gms.) were heated at 100° for 30 hours in a sealed tube, the acetone was evaporated off on a water-bath, and the 1-(2 : 4-*dichlorophenyl*)-1 : 2 : 3-*triazole*, a dark-coloured liquid which solidified on cooling, was recrystallised from boiling water, separating in long, colourless needles, m. p. 80°. It has a peculiar and very pungent smell resembling that of mushrooms. It is readily soluble in ether. Like other triazoles, it exhibits feebly basic properties and dissolves easily in strong mineral acids (Found : Cl = 33·04. $C_8H_5N_3Cl_2$ requires Cl = 33·14 per cent.).

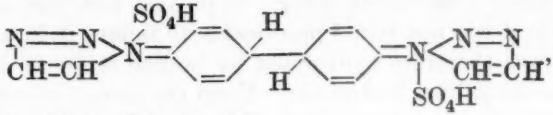
1-(2 : 5-*Dichlorophenyl*)-1 : 2 : 3-*triazole*, long, colourless needles, m. p. 78° (Found : Cl = 32·94 per cent.), 1-(2 : 4-*dibromophenyl*)-1 : 2 : 3 - *triazole*, long, colourless needles (Found : Br = 52·65. $C_8H_5N_3Br_2$ requires Br = 52·77 per cent.), and 1-o-*tolyl*-1 : 2 : 3-*triazole*, yellow, oily drops which do not solidify even on strongly cooling, were prepared similarly. They all possess a strong mushroom-like smell, and are sparingly soluble in boiling water.

1 : 1′-(4 : 4′-*Diphenylyl*)-*bis*-1 : 2 : 3-*triazole*,

$$C_2H_2N_3{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}C_2H_2N_3,$$

similarly prepared from diphenyl-4 : 4′-bisazoimide (48 hours' heating), crystallised from boiling aniline, in which it was easily soluble, in fine, pale yellow needles, m. p. 326° (decomp.) (Found :

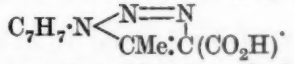
N = 29·45. $C_{16}H_{12}N_6$ requires N = 29·17 per cent.). It is a feeble base and dissolves in strong mineral acids. It dissolves in strong sulphuric acid without explosion, giving a brilliant violet colour. This is undoubtedly due to the formation of a salt with the strong sulphuric acid, the molecule assuming a di-quinonoid configuration, marked and vivid colour only being produced



when such a structure is possible.

It has been shown by Dimroth (*Ber.*, 1902, **35**, 1029) that phenylazoimide reacts with acetoacetic ester in presence of sodium ethoxide with the formation of 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid, the ester first formed being largely hydrolysed. With *o*-tolylazoimide the reaction follows a similar course, the corresponding carboxylic acid being obtained. When a halogen-substituted phenylazoimide, however, is employed, hydrolysis does not take place, and the triazolecarboxylic ester itself is the primary product of the reaction.

1-o-*Tolyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic Acid*,



—A vigorous reaction set in, and a very finely-divided, white solid separated, when sodium ethoxide (sodium 2 gms., alcohol 35 c.c.), acetoacetic ester (8 gms.), and *o*-tolylazoimide (7 gms.) were heated under reflux. After 30 minutes, the solid was collected, and dissolved in warm aqueous sodium hydroxide. From the cooled solution strong hydrochloric acid precipitated 1-o-*tolyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, which crystallised from boiling water in colourless, feathery needles, m. p. 138° (decomp.; evolution of carbon dioxide) (Found : N = 19·61. $C_{11}H_{11}O_2N_3$ requires N = 19·81 per cent.).

*Ethyl* 1-(2 : 4-*Dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*.—This experiment was similar to the preceding (10 gms. of 2 : 4-dichlorophenylazoimide). The *ester*, which separated as a colourless, crystalline solid, was obtained from boiling alcohol in colourless, flat, rhombic plates, m. p. 270° (decomp.). The yield was practically theoretical (Found : Cl = 23·45. $C_{12}H_{11}O_2N_3Cl_2$ requires Cl = 23·64 per cent.).

1-(2 : 4-*Dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, obtained by boiling the ester with aqueous sodium hydroxide and acidifying the cooled solution with dilute hydrochloric acid, crystallised from water in colourless, thin, flat, rhombic plates,

m. p. 169·5° (evolution of carbon dioxide) (Found : Cl = 26·00. $C_{10}H_7O_2N_3Cl_2$ requires Cl = 26·10 per cent.).

1 - (2 : 5 -*Dichlorophenyl*) - 5- *methyl* - 1 : 2 : 3-*triazole*-4-*carboxylic Acid*.—The white solid which separated as an amorphous pulp when 2 : 5-dichlorophenylazoimide was similarly heated with acetoacetic ester was undoubtedly 1-(2 : 5-dichlorophenyl)-5-methyl-1 : 2 : 3-triazole-4-carboxylic ester. It proved, however, so difficult to filter that it was not found practicable to isolate it in a pure dry state. It was therefore hydrolysed by boiling it for an hour with dilute aqueous sodium hydroxide. From the cooled solution strong hydrochloric acid precipitated 1-(2 : 5-*dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylic acid*, which crystallised from boiling water in minute, colourless needles, m. p. 158° (decomp.) (Found : Cl = 25·86 per cent.).

*Ethyl* 1-(2 : 4-*Dibromophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxylate*, similarly prepared from 14 gms. of 2 : 4-dibromophenylazoimide, crystallised from boiling alcohol in minute, colourless prisms, m. p. 302° (decomp.) (Found : Br = 41·04. $C_{12}H_{11}O_2N_3Br_2$ requires Br = 41·09 per cent.). On hydrolysis, it gave the corresponding *acid*, minute, glistening needles from hot water, m. p. 173° (decomp.) (Found : Br = 44·39. $C_{10}H_7O_2N_3Br_2$ requires Br = 44·29 per cent.).

1 : 1′- (4 : 4′- *Diphenylyl*)-*bis*-5-*methyl* -1 : 2 : 3 -*triazole*-4-*carboxylic Acid*.—Diphenyl-4 : 4′-bisazoimide was found to react similarly with acetoacetic ester in presence of sodium ethoxide ; but the 1 : 1′-(4 : 4′-diphenylyl)-bis-5-methyl-1 : 2 : 3-triazole-4-carboxylic ester which separated was so sparingly soluble and so difficult to filter that it was at once hydrolysed by boiling with aqueous sodium hydroxide solution as before. The sodium salt was twice recrystallised from a warm dilute solution of sodium hydroxide, from which it separated as a pulp of amorphous particles which retained water very tenaciously. The solution of the recrystallised sodium salt in boiling water was treated with hot dilute hydrochloric acid added in excess and digested on the water-bath for an hour to render the colloidal precipitate granular. The acid was thus obtained as a white, amorphous powder; from cold solutions of the sodium salt it separated in a colloidal condition. It melts at 245° with decomposition, evolving carbon dioxide (Found : N = 20·58. $C_{20}H_{16}O_4N_6$ requires N = 20·79 per cent.).

The triazolecarboxylic acids described above all melt with evolution of carbon dioxide, and are thus converted into the corresponding 5-methyltriazoles.

1-(2 : 4-*Dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole* was prepared by heating the acid (5 gms.) at 175° for ½ hour. The brown, viscid,

semi-solid mass obtained on cooling was dissolved in ether, unchanged acid removed with aqueous sodium hydroxide, and the washed, dried ethereal solution treated with sulphuric acid. The triazole sulphate, a colourless, crystalline powder, was collected and the base liberated by warm dilute sodium hydroxide solution. The yellow oil was dissolved in the minimum quantity of hot water, filtered, and allowed to cool. A few crystals obtained in a test-tube were added, to start crystallisation, as otherwise the triazole separated in oily drops which did not crystallise even on long standing. Thus obtained, it separated in colourless, compact, glistening rhombs, m. p. 69° (Found : Cl = 31·05. $C_9H_7N_3Cl_2$ requires Cl = 30·57 per cent.).

1-(2 : 5-*Dichlorophenyl*)-5-*methyl*-1 : 2 : 3-*triazole*, obtained similarly, separates from boiling water in compact, glistening rhombs, m. p. 51° (Found : Cl = 30·47 per cent.).

1-(2 : 4-*Dibromophenyl*)-5-*methyl*-1 : 2 : 3-*triazole* separates from boiling water, in which it is sparingly soluble, in small, irregular plates, m. p. 87°.

1 : 1′-(4 : 4′-*Diphenylyl*)-*bis*-5-*methyl*-1 : 2 : 3-*triazole*.—Four grams of 1 : 1′-(4 : 4′-diphenylyl)-bis-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid were heated at 255° for ½ hour. On cooling, a hard, brown, crystalline mass was obtained. This was powdered and washed first with hot dilute sodium hydroxide solution to remove traces of acid, then with water, alcohol, and ether. It was recrystallised from boiling aniline, from which it separated in colourless, flat, rhombic plates, m. p. 227°.

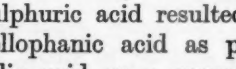
It is noteworthy that all the phenyl-1 : 2 : 3-triazoles which are unsubstituted in the triazole ring possess a strong smell resembling that of mushrooms, which is not affected by substitution in the benzene ring; the 1-phenyl-5-methyl-1 : 2 : 3-triazoles, on the other hand, are without marked odour. Thus, for example, the compounds $\begin{matrix}N{=}{=}N\\ |\\ CH{:}CH\end{matrix}\!\!>\!NX$, where X is 2 : 4-dichloro- or 2 : 4-dibromophenyl, or *o*-tolyl, possess a strong mushroom-like smell, whilst the compounds $\begin{matrix}N{=}{=}N\\ |\\ CH{:}CMe\end{matrix}\!\!>\!NX$ are almost entirely without odour of any kind.

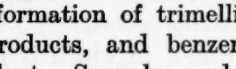
THE QUEEN'S COLLEGE, OXFORD. [*Received, March 26th*, 1924.]

# CCLVII.—*The Chemistry of Cadinene. Part I.*

By GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON.

THE dicyclic sesquiterpene cadinene forms beautifully crystalline additive compounds with the halogen acids, but so far no direct oxidation products have been obtained in crystalline form. Wallach (*Annalen*, 1887, **238**, 84; 1892, **271**, 297) found that on oxidation with chromic acid it yields a mixture of lower fatty acids, and that when heated with dilute sulphuric acid it is not hydrated but apparently is converted into an isomeric hydrocarbon. Semmler and Jonas (*Ber.*, 1914, **47**, 2076) studied the action of ozone on cadinene, but could not isolate any definite oxidation products. Ruzicka and Stoll (*Helv. Chim. Acta*, 1924, **7**, 84) found that the oxidation of the hydrocarbon with manganese dioxide and 57 per cent. sulphuric acid resulted in the formation of trimellitic acid and mellophanic acid as primary products, and benzenepentacarboxylic acid as a secondary product. Semmler and Stenzel (*Ber.*, 1914, **47**, 2558) obtained cadinene dihydrochloride by treatment of the tricyclic sesquiterpene copaene with hydrogen chloride, and from the study of the oxidation of copaene with ozone were able to state with some certainty that one of the double bonds in cadinene is adjacent to an *iso*propyl group. Finally, Ruzicka (*Helv. Chim. Acta*, 1921, **4**, 505) proved that, when dehydrogenated by heating with sulphur, cadinene is converted into the naphthalene derivative cadalene, and from the results of this and subsequent work (*ibid.*, 1924, **7**, 84) drew the conclusion that cadinene is probably to be represented by one or both of the formulæ





For our experiments cadinene was prepared by regeneration from the pure dihydrochloride, in making which it was found of advantage to use glacial acetic acid instead of ether as a solvent. No evidence of the presence of an isomeride in the cadinene thus prepared could be obtained by fractional distillation of the product. In the hope of obtaining corresponding hydroxyl derivatives, cadinene dihydrochloride, dissolved in hot glacial acetic acid, was treated with silver acetate and the product hydrolysed. We thus obtained small amounts of a saturated *compound*, $C_{15}H_{28}O_2$, and an unsaturated *compound*, $C_{15}H_{26}O$, together with cadinene itself.

The compound $C_{15}H_{28}O_2$ is perhaps a glycol, although it does not react under the usual conditions with *p*-nitrobenzoyl chloride, phthalic anhydride, or phenylcarbimide. The compound $C_{15}H_{26}O$, in solution in glacial acetic acid, yields cadinene dihydrochloride on treatment with hydrogen chloride, and by the action of a chloroform solution of bromine in the cold is converted into an unstable oily liquid which appears to be a *bromo-dibromide*, $C_{15}H_{25}OBr_3$. No esters were obtained by treatment of the compound with *p*-nitrobenzoyl chloride, phthalic anhydride, or phenylcarbimide. Taking these facts into account, it is probable that this compound is identical with the alcohol cadinol, $C_{15}H_{25}(OH)$, which was discovered in galbanum oil by Semmler and Jonas (*Ber.*, 1914, **47**, 2073).

On attempting to hydrate cadinene by Bertram and Walbaum's method, we obtained no alcohol but instead an isomeric *unsaturated hydrocarbon*, b. p. 125—128°/12 mm., which may be termed *iso-cadinene*. Unlike cadinene, this hydrocarbon does not form a stable crystalline dihydrochloride, nor does it yield a solid nitrosochloride or nitrosite. When cadinene is heated in a sealed tube with glacial acetic acid, a hydrocarbon, b. p. 124—126°/11 mm., which appears to be identical with the one just mentioned, is produced.

Tröger and Feldmann (*Arch. Pharm.*, 1898, **236**, 692) claim to have separated from oil of cade an optically inactive sesquiterpene, boiling at 250—260°, which gave no solid derivative with hydrogen chloride, and Lepeschkin (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 126) isolated from the same oil a sesquiterpene, b. p. 262—264°/760 mm., $d_4^{20°}$ 0·9204, $n_D^{20°}$ 1·5152, $[\alpha]_D$ 14·12°, which does not form crystalline products with the halogen acids and differs entirely from cadinene in chemical properties. We also have obtained from oil of cade a sesquiterpene which is very similar to this. After the crystalline cadinene dihydrochloride had been separated from oil of cade the liquid residue was heated with sodium acetate and acetic acid. A mixture of hydrocarbons was produced which consisted chiefly of a sesquiterpene, b. p. 124—128°/12 mm., $d_4^{15°}$ 0·9182, $n_D^{20°}$ 1·5166, $[\alpha]_{Hg}$ −21·9°, which does not form any solid derivatives with hydrogen chloride, and decolorises potassium permanganate much more rapidly than cadinene. As regards physical properties at least, this sesquiterpene closely resembles that described by Lepeschkin, and also that obtained by heating cadinene with acetic acid. The possible identity of these compounds is under investigation.

## EXPERIMENTAL.

*Preparation of Cadinene Hydrochloride and Cadinene.*—An attempt was made to prepare pure cadinene by fractional distillation of oil of cubebs under reduced pressure, but after a large number

of distillations the specimen obtained contained only about 70 per cent. of cadinene when tested by preparation of the dihydrochloride.

The following was the quickest and most efficient method of preparing cadinene dihydrochloride : Oil of cubebs was fractionated under reduced pressure and the fraction, b. p. 125—140°/12 mm., which contained most of the cadinene, was mixed with glacial acetic acid (⅓ vol.) and a fairly rapid stream of dry hydrogen chloride passed into the mixture. The yield was the same whether the temperature rose slightly or was kept at 0°. After keeping for 2 days at 0°, the cadinene hydrochloride was collected and recrystallised from alcohol; m. p. 118·5°. A further small quantity was obtained by concentrating the filtrate in a vacuum.

To a mixture of cadinene dihydrochloride (60 gms.) and glacial acetic acid (200 gms.) at 90°, anhydrous sodium acetate (60 gms.) was gradually added. The whole appeared to go into solution, and after a time sodium chloride began to separate. After 4 hours, the mixture was cooled, excess of water added, and the cadinene, b. p. 134—136°/11 mm., $d_4^{23°}$ 0·9189, $n_D^{20°}$ 1·5079, $[\alpha]_{Hg}$ — 125·2°, extracted with light petroleum.

The cadinene fraction, b. p. 125—140°/12 mm., of oil of cade was treated with hydrochloric acid in the same manner, and cadinene dihydrochloride, m. p. 118°, obtained. The physical constants of the regenerated cadinene were : b. p. 134—136°/11 mm., $d_4^{20°}$ 0·9185, $n_D^{20°}$ 1·5074, $[\alpha]_D$ — 130·0°.

*Action of Silver Acetate on Cadinene Dihydrochloride.*—A solution of cadinene dihydrochloride (25 gms.) in glacial acetic acid (150 gms.) at 70° was kept agitated while silver acetate (35 gms.) was added in small portions. After 1 hour, the mixture was cooled, the silver chloride filtered off and the acetic acid neutralised with sodium carbonate. The light yellow oil was collected by means of ether and hydrolysed by heating with methyl-alcoholic potash for ½ hour. The alcohol was distilled off. A portion of the residue was volatile with steam (A). After its removal, the residual liquid was treated with carbon dioxide and repeatedly extracted with ether. The viscous oil obtained from the dried extracts, on addition of a small amount of light petroleum, gave a white, crystalline solid which separated from ether in very fine, white needles, or on slow crystallisation in short prisms, m. p. 194—195° (yield 2 per cent.). Its composition agrees with that of cadinene glycol, $C_{15}H_{26}(OH)_2$ (Found : C = 74·8; H = 11·8. $C_{15}H_{28}O_2$ requires C = 75·0; H = 11·7 per cent.). The substance sublimes when heated above its m. p., is fairly easily soluble in ether or water, readily soluble in methyl or ethyl alcohol, and, in the pure state, is almost insoluble in light petroleum.

The colourless oil in the steam-distillate (A) was removed with ether and distilled under reduced pressure, the following fractions being obtained: (*a*) b. p. 134—138°/11 mm., (*b*) 138—155°/11 mm., and (*c*) 155—160°/11 mm. The fraction (*a*) consisted of cadinene (conversion into the dihydrochloride by dry hydrogen chloride in ether). The fraction (*c*), $d_4^{20°}$ 0·9741; $n_D^{20°}$ 1·5084, consisted of an unsaturated alcohol which apparently is cadinol, $C_{15}H_{25}(OH)$ (Found: C = 80·7; H = 11·5. Calc., C = 81·68; H = 11·7 per cent.). It was converted by dry hydrogen chloride in glacial acetic acid into cadinene dihydrochloride, m. p. 118°, and decolorised dilute potassium permanganate and bromine water. When the alcohol was gradually treated with bromine, both in chloroform at 0°, absorption and, to a small extent, substitution took place. The chloroform was removed under diminished pressure and an unstable, pale yellow, oily bromo-dibromide was obtained (Found: Br = 53·3. $C_{15}H_{25}OBr_3$ requires Br = 52·1 per cent.), which decomposed to a black, tarry mass on exposure to light for some hours. The fraction (*b*) of the oil consisted of a mixture of cadinene and the preceding alcohol.

When cadinene dihydrochloride was heated with silver acetate in ethereal or alcoholic solution, or was treated in ether with moist silver oxide, no cadinene glycol was obtained and the sole product appeared to be cadinene, which gave the dihydrochloride, m. p. 118°. Treatment of the dihydrobromide with silver acetate did not give an improved yield of glycol.

*Treatment of Cadinene with Hydrating Mixture.*—A solution of cadinene (5 gms. in 250 c.c. of glacial acetic acid), heated with 10 c.c. of 30 per cent. sulphuric acid on the water-bath for 8 hours, became red and finally blue. The brown oil that separated from the cooled mixture neutralised with sodium carbonate was removed with ether, and the residual liquid repeatedly extracted with ether. From the combined dried extracts an oil was obtained which did not show signs of crystallising on prolonged cooling. The greater part of it distilled with steam, the residue consisting of a resinous substance. The oil in the distillate, isolated by means of ether and purified by distillation under reduced pressure, was an unsaturated hydrocarbon, b. p. 125—128°/12 mm., $d_4^{20°}$ 0·9160, $n_D^{20°}$ 1·5141. It did not form a stable hydrochloride with hydrogen chloride in dry ether, and by treatment with bromine in cold chloroform an unstable oily bromide was produced.

*Action of Glacial Acetic Acid on Cadinene in a Sealed Tube.*—Cadinene (5 gms.) and glacial acetic acid (15 gms.) were heated together at 230—235° for 24 hours, two layers forming. The colourless oil that separated on neutralisation was removed; the residual liquid

yielded nothing to ether. The oil, purified by distillation under diminished pressure, was an unsaturated hydrocarbon, b. p. 124—126°/11 mm., $d_4^{20°}$ 0·9154, $n_D^{20°}$ 1·5158. This hydrocarbon appears to be a dicyclic sesquiterpene, and would seem to have been formed by rearrangement of the double bonds in the cadinene molecule. It is practically optically inactive, [α] — 1·0° (Found: C = 88·7; H = 11·74. $C_{15}H_{24}$ requires C = 88·2; H = 11·76 per cent.). A stable hydrochloride could not be obtained. The hydrocarbon when exposed to the air quickly resinified. It decolorised dilute potassium permanganate solution, and absorbed bromine with the evolution of hydrogen bromide, when an unstable oil containing bromine was obtained (Found: Br = 49·3. $C_{15}H_{23}Br_3$ requires Br = 54·1 per cent.). A solid nitrosochloride, nitrosite, or nitrosate could not be obtained. From the comparison of the physical constants and general behaviour, it would appear that this *iso-cadinene* is identical with the hydrocarbon obtained from cadinene when treated with hydration mixture.

*Sesquiterpene from Oil of Cade.*—The liquid obtained after the preparation of cadinene hydrochloride from the oil of cade was heated with sodium acetate in glacial acetic acid to regenerate the hydrocarbons from any liquid hydrochloride and to free the oil from hydrogen chloride. The hydrocarbons were then separated and subjected to fractional distillation under reduced pressure, when a main fraction (b. p. 124—128°/12 mm., $d_4^{15°}$ 0·9182, $n_D^{20°}$ 1·5166, $[\alpha]_{Hg}$ — 21·9°) was obtained. When the oil was treated with hydrogen chloride, no cadinene dihydrochloride could be obtained, and it did not form a stable hydrochloride. This hydrocarbon quickly decolorised potassium permanganate in the cold, but no solid derivatives have so far been obtained.

We desire to express grateful thanks to the Carnegie Trust for assistance which enabled us to carry on this work.

UNIVERSITY OF GLASGOW. [*Received, June 3rd,* 1924.]

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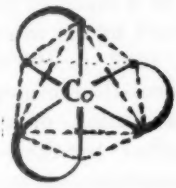
## CCLVIII.—*Researches on Residual Affinity and Co-ordination. Part XXII. Optically Active Salicylatocobalt Diethylenediammines.*

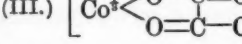
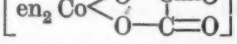
By GILBERT T. MORGAN and J. D. MAIN SMITH.

THE existence of enantiomorphous isomerides of octahedral symmetry was demonstrated by Werner (*Ber.*, 1912, **45**, 121; 865; 1228; *Helv. Chim. Acta*, 1920, **3**, 472), who resolved into optically

active antipodes the triethylenediammines of cobalt, chromium, rhodium, and iridium. Similar resolutions were accomplished by Werner and others of the trioxalato-salts of cobalt (III), chromium,

(I.)  (II.)

rhodium, iridium, and iron (Werner, *Ber.*, 1912, **45**, 3061; 1914, **47**, 1954; Delépine, *Compt. rend.*, 1914, **159**, 239; Jaeger and Thomas, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 215; Thomas, J., 1921, **119**, 1140), and Werner was also successful in obtaining optically active isomerides containing two ethylenediamine molecules and a bivalently bound acidic chelate group in the co-ordination nucleus, as in the monocarbonato-, monooxalato, and monomalonato-series (IV., *Ber.*, 1912, **45**, 3281).

(III.)   (IV.)

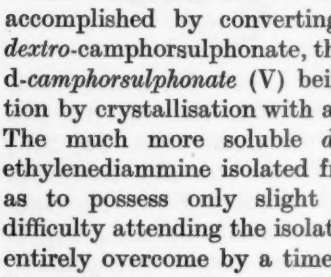
These enantiomorphs of mixed type were, however, produced, not by resolution from their racemoid isomerides, but by substitution from previously resolved *dextro-* and *lævo*-dichlorodiethylenediammines and analogous salts (*Ber.*, 1911, **44**, 3279).

We have now succeeded in resolving a racemoid complex of this mixed type containing two ethylenediamine molecules and one unsymmetrical acidic chelate group by an extension of our former researches on salicylatocobaltammines (J., 1922, **121**, 1956; 1923, **123**, 1096). These salts, which contain tervalent cobalt co-ordinated with four ammonia molecules and a bivalent salicylato-radical, should not exhibit stereoisomerism, and in order to produce an octahedral type of enantiomorphism 2 mols. of ethylenediamine have been substituted for the four ammonias. The inactive racemoid salts, [Sal.Co2en]X, have been synthesised in the following ways:

(1) By direct nuclear substitution of ammonia by ethylenediamine in the salicylatocobaltammines, [Sal.Co4$NH_3$]X; (2) by oxidising cobaltous salts with hydrogen peroxide in presence of ethylenediamine hydrate and salicylic acid; (3) by nuclear substitution of the salicylato-radical in one of the following cobalt ethylenediammines:—*cis-* and *trans*-dichlorocobalt ethylenediammines, [$en_2$ $CoCl_2$]X, aquohydroxocobalt ethylenediammines, [$en_2$ $CoH_2O$,OH]$X_2$, or dihydroxocobalt ethylenediammines, [$en_2$ $Co(OH)_2$]X.

Except in the last case of dihydroxodiethylenediammine salts, the products were always contaminated with yellow (luteo) triethylenediamminocobaltic chloride, $[en_3\,Co]Cl_3$. But even when not isolated in a state of purity the salicylato-compound could always be detected by its intense green coloration with warm nitric acid (*loc. cit.*, 1922, p. 1969), this reaction being characteristic for all salicylatocobaltammines and salicylatocobalt ethylenediammines.

The resolution of the racemoid chloride, [Sal.Co2en]Cl, was accomplished by converting it successively into carbonate and *dextro*-camphorsulphonate, the l-*salicylatodiethylenediamminocobaltic* d-*camphorsulphonate* (V) being readily obtained from aqueous solution by crystallisation with a mixture of alcohol, acetone, and ether. The much more soluble *d*-camphorsulphonate of the *d*-cobalt ethylenediammine isolated from the mother-liquors was so impure as to possess only slight optical activity. The experimental difficulty attending the isolation of the enantiomorph was, however, entirely overcome by a timely and generous gift of *l*-camphor and its sulphonic acid, for which we express our indebtedness to Sir William Pope. With these reagents, which are no longer obtainable commercially, it was readily possible to isolate d-*salicylatodiethylenediamminocobaltic* l-*camphorsulphonate* (VI).

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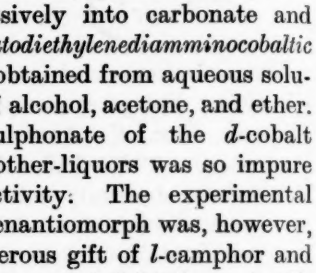
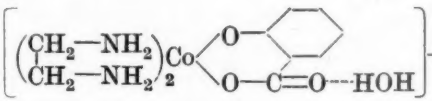



(VI.)

The resolution of these two camphorsulphonates into a condition of complete optical purity was unnecessary, since on treatment with aqueous sodium mercurichloride or mercuribromide any racemoid mercurihalide remaining was deposited immediately, whereas the more soluble *d*- or *l*-salts crystallised slowly from the filtrate. These optically active mercurihalides retained their activity unimpaired when crystallised from boiling water or after keeping in dilute solution for 6 weeks. This stability offers a marked contrast to the more or less rapid racemisation generally observed in the case of optically active salts of the oxalato- or malonato-series.

The malonato- and salicylato-salts both contain 6-membered acidic chelate groups, but the greater stability of the salicylato-series is probably due to the non-ionisable character of the phenolic junction with the metal.

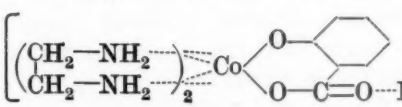


(VII.)

The salicylatodiethylenediamminocobaltic salts are very similar to the corresponding ammoniated salts in colour, crystalline form, and chemical properties. They differ from the ammoniated series, however, in being much more soluble in water or aqueous alcohol, and consequently the analogy formerly noticed between the salicylatocobaltammines and sodium salts is no longer apparent in the salicylatocobalt diethylenediammines. For instance, the bicarbonate of the new series is much more soluble than the carbonate.

Nevertheless, the two groups display one noteworthy resemblance as regards the hydration of their normal and acid salts, respectively. In the salicylatocobaltammines, the normal salts contain 1 mol. of firmly bound water per complex cation, whereas the acid or hydrogen salts are either anhydrous or contain only loosely held water which is eliminated below 100°. A similar contrast has been noticed in the new salicylatocobalt diethylenediammines. The bicarbonate and hydrogen dinitrate are anhydrous, the latter being stable in air whereas the normal nitrate is highly deliquescent, both being similar in this respect to the corresponding tetrammine nitrates. In both series the acid chlorides are exceptional in being hydrated, although the water is only feebly held, and probably by the anion, for on aqueous hydrolysis the excess of acid is removed together with a portion of the water, when the less soluble and less hydrated normal chloride slowly separates.

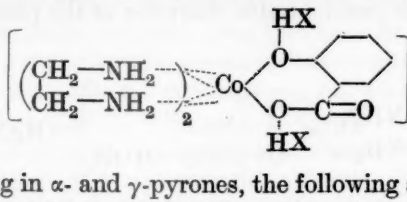
These results confirm the former deductions (J., 1923, **123**, 1097) in regard to the presence in these salicylatocobaltammines of a binuclear co-ordination complex of mixed polarity, the cobalt giving a positive focus whereas an oxygen atom furnishes a negative focus. The circumstance that only one molecule of water (VIII; R = HOH) or one hydrion (VIII; R = HX) is implicated in the



(VIII.)

complex cation confirms the assumption that the water or hydrogen is attracted to the unique carbonyl oxygen and not to either of the

hydroxylic oxygens. (IX). Moreover, since these salicylato-complexes contain oxygen atoms in a state of combination similar to

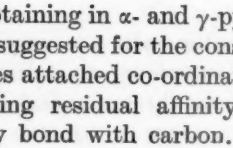



(IX.)

that obtaining in α- and γ-pyrones, the following analogous explanation is suggested for the constitution of oxonium salts :—the hydrion becomes attached co-ordinatively to the carbonyl oxygen, this atom possessing residual affinity in virtue of its unsaturated double valency bond with carbon.

## Experimental.

I. *Racemic Normal Salts.* (Formula VIII).




= Y, en = $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$.

*Chloride dihydrate,* $YCl(H_2O)_2$ :—*trans*-Dichlorodiethylenediamminocobaltic chloride (41 gms. = 1 mol.), prepared from the hydrated acid praseo-salt by heating at 105° was triturated with silver oxide from 48 gms. of silver nitrate (= 2 atoms Ag) in 100 c.c. of water until the colour changed from green to purple. Reaction was completed after 15 minutes on the water-bath. To the filtrate containing *cis*-dihydroxo-chloride were added 19·7 gms. of salicylic acid (1 mol.); the magenta-red solution of diaquo-chloride salicylate darkened on evaporation with the formation of the salicylato-chloride. At this stage pink needles of *disalicylatodiethylenediamminocobaltic salicylate* (p. 2004) separated, the yield being 4 gms., or 5 per cent. The filtrate evaporated to a small bulk yielded two crops of dark red crystals, which were washed with alcohol and ether and recrystallised from hot water (40·5 gms. or 72 per cent.). 0·2000 gave 0·2510 $CO_2$; 0·1158 $H_2O$; C = 34·2, H = 6·43. 0·4910 gave 0·870 $NH_3$; N = 14·6. 0·4626 gave 0·1736 AgCl; Cl = 9·28. 0·5922 gave 0·2408 $CoSO_4$; Co = 15·5. 0·5922 lost 0·0256 $H_2O$; $H_2O$ = 4·46. $C_{11}H_{20}O_3N_4ClCo,2H_2O$ requires C = 34·2; H = 6·21; N = 14·5; Cl = 9·18; Co = 15·3; $1H_2O$ = 4·66 per cent.

*Salicylatodiethylenediamminocobaltic chloride dihydrate,* purplish-red, 6-sided plates, losing half the combined water at 100° and nothing further at 120°, was extremely soluble in water to a neutral, dark red solution. Silver nitrate yielded silver chloride (presence of ionised chlorine), but no silver salicylate on prolonged boiling. There was no coloration with ferric chloride (absence of salicylate-

ion), and salicylic acid was eliminated only by hot concentrated acids or caustic alkalis. Warm 5*N*-nitric acid gave the intense green coloration characteristic of salicylatocobaltammines.

*Carbonato dihydrate*, $Y_2CO_3(H_2O)_2$, was prepared from an aqueous solution of the foregoing salt and excess of silver carbonate, the filtrate being concentrated and treated with alcohol :—0·1978 gave 0·03697 $NH_3$; N = 15·4. 0·2078 gave 0·0886 $CoSO_4$; Co = 16·2. Eqt. wt. = 359. $C_{23}H_{40}O_9N_9Co_2,2H_2O$ requires N = 15·4; Co = 16·3 per cent.; eqt. wt. = 363.

This carbonate crystallised from dilute alcohol in violet-red, rhomboidal plates sparingly soluble in cold water; the dark red solution was alkaline to methyl-orange and bromophenol-blue and gave immediate precipitates with soluble calcium, mercuric, and silver salts.

*Nitrate trihydrate*, $YNO_3(H_2O)_3$, was obtained from the foregoing carbonate and calculated 2*N*-nitric acid on precipitation with mixed alcohol–acetone–ether. Yield 40 per cent. 0·5244 gave 0·1906 $CoSO_4$; Co = 13·8; and lost 0·0432 $H_2O$ at 100°; $H_2O$ = 8·24. $C_{11}H_{20}O_6N_5Co,3H_2O$ requires Co = 13·7; $2H_2O$ = 8·35 per cent. The nitrate crystallised in dark red needles, deliquescing immediately on exposure to air and was dried over fused calcium chloride.

*Mercurichloride hydrate* (formula VII) was obtained in 67 per cent. yield from the calculated amounts of the foregoing chloride and mercuric chloride in dilute aqueous solution. 0·4290 gave 0·04484 $NH_3$; N = 8·61. 0·3988 gave 0·2692 AgCl; Cl = 16·7. 0·4504 gave 0·1088 $CoSO_4$; Co = 9·20. 0·4652 gave 0·1460 Hg; Hg = 31·4. $C_{11}H_{20}O_3N_4Cl_3CoHg,H_2O$ requires N = 8·75; Cl = 16·6; Co = 9·22; Hg = 31·3 per cent. This racemoid mercurichloride, being very sparingly soluble in water, is precipitated, on mixing saturated solutions of the lævo- and dextro-components, in purplish-red plates or flattened needles, soluble in an equivalent proportion of 5*N*-hydrochloric acid. The acid mercurichloride was not isolated.

*Mercuribromide hydrate* (formula VII) was obtained in 71 per cent. yield from the carbonate, hydrobromic acid, and mercuric bromide in dilute aqueous solution. It crystallised from hot water in sparingly soluble, purplish-red, flattened needles. 0·3680 gave 0·03146 $NH_3$; N = 7·04. 0·5092 gave 0·3688 AgBr; Br = 30·8. 0·3338 gave 0·0680 $CoSO_4$; Co = 7·76.

$C_{11}H_{20}O_3N_4Br_3CoHg,H_2O$ requires N = 7·24; Br = 31·0; Co = 7·63 per cent. It is slightly soluble in warm 10*N*-hydrobromic acid (but no acid mercuribromide forms), and is decomposed by 33*N*-acid with elimination of salicylic acid and formation of green *trans*-dibromodiethylenediamminocobaltic bromide (praseo-salt).

*Mercuri-iodide hydrate* (formula VII) was obtained in quantitative

yield from aqueous solutions of salicylato-chloride and sodium mercuri-iodide in dark purple-red, flattened needles, very sparingly soluble in water. 0·5836 gave 0·4480 AgI; I = 41·5. 0·3524 gave 0·0596 $CoSO_4$; Co = 6·44. 0·5072 gave 0·1108 Hg; Hg = 21·8. $C_{11}H_{20}O_3N_4I_3CoHg,H_2O$ requires I = 41·7; Co = 6·45; Hg = 21·9 per cent.

II. *Optically Active Normal Salts* (Formulæ V and VI).

*Salicylatodiethylenediamminocobaltic Camphorsulphonates*, $YC_{10}H_{15}O_4S(H_2O)_2$.

—1. lævo-*Base* dextro-*camphorsulphonate*, bright red, six-sided plates (two crops = 5·2 gms.), separated slowly on adding alcohol, 15 c.c., ether, 15 c.c., and acetone, 30 c.c., to 10·9 gms. of racemoid carbonate and 7·0 gms. of *d*-camphorsulphonic acid (Reychler) in 15 c.c. of water. 0·4088 gave 0·1086 $CoSO_4$; Co = 10·1. 0·4408 lost 0·0124 $H_2O$; $H_2O$ = 2·81. $C_{21}H_{35}O_7N_4SCo,2H_2O$ requires Co = 10·1; $H_2O$ = 3·09 per cent. Aqueous solutions were transparent only to a narrow band in the darker red spectrum with a maximum about the lithium line 6708 Å. ($10^{-8}$ cm.). Light from this source was used throughout these measurements. Recrystallisation of the various fractions failed to increase the optical activity, the maximum being obtained in the first and second crops. The final crops showed only small rotation of opposite sign, indicating that the dextro-salt of the dextro-base was not being obtained in quantity sufficient to complete the resolution into both components. Owing to the intensity of colour, solutions stronger than 2 per cent. in 0·5-dcm. tube could not be used. The first two crops of *l*-base *d*-camphorsulphonate gave $[\alpha]_{Li\ 6708}$ − 41·3°, whence $[M]_{Li}$ − 240·4° and $[M]$ for the cobaltammine ion − 290·4°.

2. dextro-*Base* lævo-*camphorsulphonate* was prepared in the same way as the preceding isomeric salt, using *l*-camphorsulphonic acid. 0·8182 gave 0·2196 $CoSO_4$; Co = 10·2; and lost 0·0224 $H_2O$; $H_2O$ = 2·74 $[\alpha]_{Li\ 6708}$ + 33°, whence $[M]$ + 192·1° and $[M]$ for cobaltammine ion + 242·1°.

1-*Salicylatodiethylenediamminocobaltic mercurichloride hydrate* (formula VII) was obtained in 80 per cent. yield from concentrated aqueous solutions of *l*-base *d*-camphorsulphonate and sodium mercurichloride. On recrystallising from hot water, a small amount of racemic mercurichloride separated, the purified *lævo*-salt crystallising during 3 hours. 0·4692 gave 0·3166 AgCl; Cl = 16·7. 0·4000 gave 0·0970 $CoSO_4$; Co = 9·23. 0·4692 gave 0·1464 Hg; Hg = 31·2. $C_{11}H_{20}O_3N_4Cl_3CoHg,H_2O$ requires Cl = 16·6; Co = 9·22; Hg = 31·3 per cent. The purple-red prisms are much darker in colour than the racemic salt and much more soluble in water. The

solubility in cold water is less than 1 per cent., but owing to the slow rate of crystallisation 2 per cent. solutions can be examined polarimetrically :—$[\alpha]_{Li\ 6708}$ — 46°, whence $[M]_{Li}$ — 294·4°.

d-*Salicylatodiethylenediamminocobaltic mercurichloride hydrate* (formula VII) was obtained from *d*-base *l*-camphorsulphonate as in the preceding preparation. 0·4828 gave 0·3266 AgCl; Cl = 16·7. 0·4342 gave 0·1074 $CoSO_4$; Co = 9·42. 0·4828 gave 0·1498 Hg·Hg = 31·2. $[\alpha]_{Li\ 6708}$ + 45°, whence $[M]_{Li}$ + 288·0°.

l-*Mercuribromide hydrate* (formula VII), obtained similarly to the dextro-mercurichloride by the use of sodium mercuribromide in dilute aqueous solution, formed dark purplish-red to black plates considerably more soluble in water than the racemoid salt; in cold water, only 1 per cent. solution was obtainable. 0·2288 gave 0·0464 $CoSO_4$; Co = 7·72. $C_{11}H_{20}O_3N_4Br_3CoHg,H_2O$ requires Co = 7·63 per cent. $[\alpha]_{Li\ 6708}$ — 38°, whence $[M]_{Li}$ — 294°.

d-*Mercuribromide hydrate* (formula VII) was obtained similarly to the preceding compound and was identical in chemical properties. 0·2952 gave 0·0589 $CoSO_4$; Co = 7·60 per cent. $[\alpha]_{Li\ 6708}$ + 38°, whence $[M]_{Li}$ + 294°.

### III. *Racemoid Hydrogen Salts* (Formula IX).

*Salicylatodiethylenediamminocobaltic hydrogen dichloride trihydrate*, $YHCl_2(H_2O)_3$, was obtained in 84 per cent. yield on adding equal volumes of alcohol, acetone, and ether to 8·7 gms. of the normal chloride (p. 2000) in 4 c.c. of water and 1·0 c.c. of 10*N*-hydrochloric acid. 0·4312 gave 0·0672 $NH_3$; N = 12·9. 0·2356 gave 0·1524 AgCl; ionic Cl = 16·1. 0·4340 gave 0·1512 $CoSO_4$; Co = 13·3. Eqt. wt. = 453. $C_{11}H_{20}O_3N_4Cl_2H,3H_2O$ requires N = 12·7; Cl = 16·1; Co = 13·4 per cent.; eqt. wt. = 441. It formed scarlet, six-sided plates stable in air, but extremely soluble in water to strongly acid solutions. When dissolved in a small amount of water or aqueous pyridine, the solution changed from scarlet to carmine, the normal chloride slowly separating.

*Hydrogen dinitrate*, $YH(NO_3)_2$, was obtained in 40 per cent yield on adding alcohol, 1 vol.; acetone, 1 vol.; and ether, 4 vols., to a concentrated solution of either the normal nitrate with one equivalent of 7·5*N*-nitric acid or the normal carbonate with two equivalents of nitric acid. 0·2656 gave 0·0930 $CoSO_4$; Co = 13·7. 0·4014 gave 0·1142 $HNO_3$; $NO_3$ = 28·0. Eqt. wt. = 446. $C_{11}H_{20}O_3N_4Co(NO_3)_2H$ requires Co = 13·4; $NO_3$ = 28·2 per cent.; eqt. wt. = 440. It formed dark red plates stable in air, and very soluble in water to strongly acid solutions which did not develop the specific intense green coloration until after the addition of another equivalent of nitric acid.

*Hydrogen carbonate,* $YHCO_3$, was obtained in 80 per cent. yield on adding an equal volume of acetone to a concentrated aqueous solution of the normal carbonate saturated with carbon dioxide. 0·4280 gave 0·07865 $NH_3$; N = 15·1. 0·3938 gave 0·1660 $CoSO_4$; Co = 16·0. Eqt. wt. = 377. $C_{11}H_{20}O_8N_4CoHCO_3$ requires N = 14·9; Co = 15·7 per cent.; eqt. wt. = 376. It formed bright red, diamond-shaped and six-sided plates, much more soluble in water than the normal carbonate. The dark red solution was neutral to litmus and phenolphthalein, but alkaline to methyl-orange and bromophenol-blue. Cold aqueous solution gave no precipitate with mercuric or calcium salts until after boiling.

IV. *Disalicylatodiethylenediamminocobaltic salicylate,* $[en_2\,Co(C_7H_5O_3)_2]C_7H_5O_3$,

the by-product in the preparation of salicylatodiethylenediamminocobaltic chloride, was obtained only with excess of salicylic acid or when this reagent was rapidly added. 0·4016 gave 0·1068 $CoSO_4$; Co = 10·1. $C_{25}H_{31}O_9N_4Co$ requires Co = 10·0 per cent. It formed pale violet-pink, slender needles, insoluble in water, gave a purple coloration with ferric chloride (salicylate ion), lost no weight at 100°, and developed no green coloration with warm nitric acid (absence of the salicylatocobaltammine complex); with boiling concentrated hydrochloric acid, it yielded green *trans*-dichlorodiethylenediamminocobaltic chloride (praseo-salt) with elimination of salicylic acid.

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## CCLIX.—*Metallic Hydroxy-acid Complexes. Part III. The Constitution of Cuprimalates and Analogous Compounds.*

By IAN WILLIAM WARK.

IN this communication an attempt is made to show that the ordinary views of primary valence lead to a satisfactory explanation of the structure of cuprimalic acid and its salts (J., 1923, **123**, 1826), and, in addition, of many other copper complexes. No absolute

proof is offered that Werner's ideas on inner metallic complexes (see Part I, J., 1923, **123**, 1815) are inapplicable here; all that is claimed is that the theory presented, whilst not involving any new assumptions about valencies, affords a very simple and complete account of the nature of metallic hydroxy-acid complexes and suggests many lines for future research. Later, when time permits of an examination of the copper hydroxide–monoalkyl malate derivatives, crucial experiments can be planned in order to make possible an absolute choice between the two rival theories.

*Constitution of the Cuprimalates.*—Measurements of the apparent molecular weight in solutions of ammonium and sodium cuprimalates indicate an association, but they do not warrant the assumption that cuprimalic acid is dibasic, for the molecular weights decrease much too rapidly with dilution. No conclusions as to the basicity may be drawn from measurements in a solution of the acid itself, since the high value of the copper-ion concentration proves that it is almost completely converted into the isomeric normal cupric malate when dissolved in water. The author considers that the acid is a monobasic one and that these associations are of the same loose type that acetic acid undergoes in benzene solution.

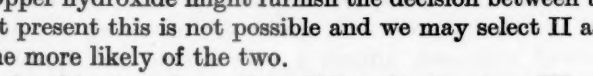
Since the alkali metal cuprimalates are neutral, it is almost certain that the alkali metal occupies a position in the carboxyl group. If it replaced the hydrogen atom of an alcoholic hydroxyl group, the compound would most probably be alkaline.

Beilstein ("Organische Chemie," 4th ed., III, p. 423) suggests that in the compound present in a solution of cupric malate in caustic soda the copper occupies a position in the hydroxyl group. According to this view, the constitution of the cuprimalates would be of the type $M'O_2C{\cdot}CH_2{\cdot}CH(O{\cdot}Cu{\cdot}OH){\cdot}CO_2H$, or $M'{\cdot}CuC_4H_5O_6$. Grossmann and Loeb (*Z. Ver. Deut. Zuckerind.*, 1908, 994) suggested, on the other hand, that the compounds possess the constitution $M'O_2C{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2{\cdot}Cu{\cdot}OH$, or $M'{\cdot}CuC_4H_5O_6$. Completely dehydrated sodium cuprimalate, however, has the composition $Na{\cdot}CuC_4H_3O_5$,—the ammonium salt and the acid itself, when dehydrated as far as possible, are of similar composition—and therefore it is necessary to withdraw the elements of one molecule of water from either of the suggested formulæ before it will fit the experimental facts. The only reasonable way in which to effect this elimination is to use copper as a connecting link between carboxylic and alcoholic hydroxyl groups. The compound must therefore be of the type I or the isomeric type II.

(I.) $NaO_2C{\cdot}\underset{\displaystyle O-Cu-O}{\underset{|}{\overset{|}{C}}}H{\cdot}CH_2{\cdot}CO$ $\qquad$ $NaO_2C{\cdot}CH_2{\cdot}\underset{\displaystyle O{\cdot}Cu{\cdot}O}{\underset{|}{\overset{|}{CH}}}-CO$ (II.)

A study of the action of the two isomeric monoalkyl malates on copper hydroxide might furnish the decision between these formulæ. At present this is not possible and we may select II as being rather the more likely of the two.

On this view the acid itself has the structure III. The isomeric change from cupric malate to cuprimalic acid consists merely in the wandering of a hydrogen atom:




Henderson, Orr, and Whitehead (J., 1899, **75**, 542) isolated a complex molybdenum compound, $MoO_2 \cdot C_4H_3O_5Na$, for which they suggested a structure similar to II ($MoO_2$ replacing Cu).

Structures analogous to that suggested for the copper compound can be assigned to all the other malic acid complexes which have been mentioned in Part II.

Although a solution of a compound of this type, containing its copper as one atom of a five-membered ring,—as pointed out by Werner, such rings containing carbon are notoriously stable—might be expected to yield only a very low concentration of copper ions, a partial splitting of the ring must occur to provide the small concentration of copper-ions which experiment has proved is present. There is no possibility of ring formation in the neutral complexes derived from the monohydroxy-monobasic acids, for in these, as was shown in a paper on cuprilactates (J., 1923, **123**, 1815), all the carboxylic hydrogen is replaced by alkali metal and it is very probable that copper replaces the hydrogen atoms of two alcoholic hydroxyl groups. It is significant that the stability of these complexes is much less than that of the corresponding compounds formed by tartaric, glyceric, and other acids where the ring is, at any rate, a theoretical possibility. This view of the nature of the complexes also accounts for the non-existence of malic acid complexes with the univalent metals.

*Extension of the Theory to Alkaline Complexes.*—In addition to providing a satisfactory account of the cuprimalates, the idea that copper may replace one atom of hydrogen in a carboxyl group and another in an alcoholic hydroxyl group may be applied to explain the properties of certain alkaline copper-containing complexes. Very few alkaline compounds of this type have yet been isolated in pure crystalline form and until they have been prepared in an unquestionable state of purity or their composition satisfactorily established in some other way, it is useless to attempt to consider their structures. There are a few exceptions the compositions of

which may be taken as thoroughly established; the constitutions of one or two of these is now discussed.

A cupricitrate first described by Luff (*Z. Ges. Brauwesen*, **21**, 319) has the composition $(C_6H_4O_7)_2K_6Cu,6H_2O$ and readily loses all six molecules of water on heating. At first it was assumed that the copper replaced the hydrogen atoms of the hydroxyl groups of a pair of potassium citrate molecules—$K_3C_6H_5O_7$. But, as Pickering (J., 1910, **97**, 1837) pointed out, since the compound is strongly alkaline, this view is unsatisfactory. The structures he proposed, involving quadrivalent copper, and often containing a molecule of water more than the facts justify, are untenable.

The ideas now presented lead to the structure

$$(CO_2K\cdot CH_2)_2C(\overset{b}{O}K)\cdot CO\cdot O\cdot Cu\cdot O\cdot C(CH_2\cdot CO_2K)_2\cdot CO_2K,$$

in which the potassium atom *b*, replacing as it does the hydrogen atom of an alcoholic hydroxyl group, gives to the compound its alkaline quality.

Pickering (J., 1911, **99**, 1347) has described an alkaline cupriglycollate, $C_4H_4O_6CuK_2,2H_2O$, from which both water molecules are readily removed. The structure he suggested is such that these two molecules could not easily be lost; that which is now proposed, $OK\cdot CH_2\cdot CO_2\cdot Cu\cdot O\cdot CH_2\cdot CO_2K,2H_2O$, seems to fit the facts better.

Bullnheimer and Seitz (*Ber.*, 1900, **33**, 817) described certain alkaline derivatives of tartaric acid of the type $M'_2CuC_4H_2O_6$, and Kahlenburg (*Z. physikal. Chem.*, 1895, **17**, 557) has shown that their alkalinity (as measured by the hydroxyl-ion concentration) corresponds to only one of the two sodium atoms. The structure $CO_2M\cdot CH(OM)\cdot CH<\begin{matrix}CO\cdot O\\ O—Cu\end{matrix}$ affords an explanation of their properties.

*Constitution of Compounds of the Tartar Emetic Type.*—It was pointed out in the paper on cuprilactates that no general conclusion has been drawn about the structure of tartar emetic. A study of the properties of this compound and of similar derivatives of tartaric acid leads to the conclusion that there must exist an (hypothetical) acid, of which these derivatives are salts, and that this acid and its salts show a striking resemblance to cuprimalates and their parent acid. It has been suggested that the latter owe their stability to the presence of a five-membered ring, and so it is natural to regard the antimony complexes, the antimony-ion concentration of which has been shown by Kahlenburg (*loc. cit.*) to be very low, as possessing an analogous constitution. The formula suggested by Schiff for tartar emetic, $KO_2C\cdot CH(O)\cdot CH(O)\cdot CO$ with O, O, O bonded to Sb, meets these require-

ments, and is, moreover, the only one of the formulæ proposed which agrees with the composition of the completely dehydrated compound.

*Constitution of the Neutral Cupritartrates.*—The ideas advanced up to the present are inadequate to account for the constitution of the neutral cupritartrates. It was shown (Packer and Wark, J., 1921, **119**, 1348) that their composition may be expressed in the empirical form $(M'\cdot CuC_4H_3O_6)_n,CuO$, where $n$ may have the value 2 or 3. However applied, the theory—as developed to this stage—leaves the extra CuO group unaccounted for. It is purely a matter of conjecture as to where this group must be linked. It is perhaps more than a coincidence that the neutral cupritartrates bear to the simpler cuprimalates exactly the same relation that the compounds containing the familiar " condensed anions " bear to the simpler inorganic oxy-salts, and the author is inclined to regard them as of analogous constitution to these condensed anion compounds.

## *Conclusions.*

A theory has been presented which gives a satisfactory explanation of the structure of the cuprimalates and allied cupric complexes. In Part I, it was shown how any theory which is applicable to the compounds formed by copper can easily be extended to the similar compounds formed by other metals and also to those formed by the non-metals as well. Thus it will be seen that if the ideas advanced in this paper can withstand the test of further experimental work, a general theory of the constitution of the complexes formed by the hydroxy-acids and the higher alcohols will have been established.

It has been necessary to assume the existence of two distinct classes of neutral complexes. One of these is exemplified in the compounds from the monobasic-monohydroxy-acids such as lactic and salicylic acids, and in them it is thought that copper replaces the hydrogen atoms of two hydroxyl groups. All the complexes formed by the alcohols themselves belong to this class. The other class includes the cuprimalates and many other neutral and alkaline complexes. In these, it is assumed, a copper atom replaces the hydrogen atom of an alcoholic hydroxyl group and the hydrogen atom of a carboxyl group.

In order further to test these views work will be undertaken with other acids, and the author hopes soon to be able to investigate the mandelic, hydroxymalonic, and glyceric acid complexes. It is thought that a study of the action of alkalis on the copper amino-acid complexes will also prove of interest.

In conclusion, the author expresses his thanks to Professor Donnan for his interest and advice during the progress of the work, and to the Royal Commissioners of the Exhibition of 1851 for a scholarship which has enabled him to pursue it.

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UNIVERSITY COLLEGE, LONDON. [*Received, June 22nd,* 1923.]

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## CCLX.—*A Direct Method for the Estimation of Glucose and Other Carbohydrates.*

By EDMUND KNECHT and EVA HIBBERT.

THE chemical methods for the estimation of glucose and other "reducing" sugars are based upon the determination of their reducing capacity on a standard alkaline copper or mercury solution. Of such solutions, that originally recommended by Fehling is the one usually employed. In all these estimations, the reactions do not take place in any stoicheiometric proportions, the calculations of the results being based on factors which have been determined empirically for each individual sugar.*

It has been shown (this vol., p. 1537) that phenylglucosazone can be estimated with accuracy by reduction with excess of standard titanous chloride in presence of sodium tartrate, followed by a back-titration with crystal-scarlet to ascertain the amount of reducing agent in excess. The amount of reducing agent required for 1 mol. of glucosazone was found to be equivalent to 6H. The only further requirement to render the titration practically useful was a quantitative conversion of the glucose into its osazone. Former work on this subject (Knecht and Thompson, this vol., p. 222) had shown that by employing glucose and phenylhydrazine in the proportions recommended by Emil Fischer it was not possible to obtain a yield of glucosazone higher than 83 per cent. It was, however, ascertained incidentally that, by increasing the amount of phenylhydrazine beyond the proportion usually employed, a somewhat higher yield of osazone resulted. The observation was not carried to its logical conclusion at the time, but it is now found that if in place of using 3 mols. of phenylhydrazine to 1 mol. of glucose (the amount theroetically required), the amount of phenylhydrazine is increased to 12 mols., the reaction becomes quantitative. The osazone formed can be titrated directly, without being isolated. A further advantage

* Willstätter and Schudel's modification of Romijn's process (*Ber.*, 1918, 51, 780), in which oxidation of the glucose is effected by means of sodium hypoiodite, is stoicheiometrically accurate, but is only applicable to aldoses.

in using such a large proportion of phenylhydrazine is achieved, in that the time required for the reaction to go to completion is only 10 minutes.

A direct proof of the quantitative character of the glucosazone formation was not feasible by gravimetric means, owing to the not inconsiderable solubility of the osazone in the large excess of phenylhydrazine acetate. By weighing the glucosazone which had separated and estimating by titration what remained in solution in the filtrate, it was, however, possible to account for the whole. 0·3321 Gm. of glucose gave 0·6296 gm. of glucosazone; the filtrate contained 0·02979 gm., which when added together and calculated in terms of glucose represent a total of 99·7 per cent.

The procedure adopted is to dissolve 0·1—0·2 gm. of glucose in water and make up to 100 c.c. To 10 c.c. of this solution, 1 c.c. of a saturated solution of sodium tartrate, and a solution of 0·25 gm. of phenylhydrazine in acetic acid are added, the mixture is heated for 10 minutes on a briskly boiling water-bath, a known volume of standard titanous chloride solution (which must be in considerable excess) is added, and the solution boiled for 1—2 minutes over a free flame while a current of carbon dioxide is passed into the flask. The excess of titanous chloride is ascertained by titrating the hot solution, after the addition of excess hydrochloric acid, with a solution of crystal-scarlet standardised against the titanous chloride solution, a permanent red colour indicating the end of the reaction. The time required for a complete estimation is about 20 minutes. Lævulose is estimated in exactly the same way as glucose, and the same method holds good for sucrose after inversion. But unless the acid has been partly neutralised after inversion, it is advisable to increase the proportion of sodium tartrate before forming the osazone.

Since lactose and maltose both form osazones with phenylhydrazine, it is not necessary to invert them before carrying out an estimation. That the osazones of these two sugars behave in a similar way to those of glucose and lævulose towards titanous chloride is shown from the following data.

*Maltosazone* was prepared and obtained pure (m. p. 205°) by crystallisation from hot dilute alcohol.

0·1098 Gm. required, on reduction and back-titration with crystal-scarlet, 20·1 c.c. of titanous chloride (of which 1 c.c. = 0·003521 gm. Fe). Assuming that $C_{24}H_{32}O_9N_4$ requires 6H, this represents 99·7 per cent. of osazone.

*Lactosazone*, prepared in the usual way and purified by crystallisation from dilute alcohol, showed m. p. 206°.

0·1012 Gm. required, on reduction and back-titration with crystal-

scarlet, 18·4 c.c. of titanous chloride (of which 1 c.c. = 0·003546 gm. Fe). And assuming the reduction to take place as with maltosazone, this gives 99·75 per cent.

*Proofs of Method.—Glucose.* 0·9728 Gm. of pure glucose was dissolved in water and made up to 1 litre. 25 C.c. were heated with 5 c.c. of acetic acid, 1 gm. of phenylhydrazine, and 1 c.c. of a saturated solution of sodium tartrate, on a water-bath for 10 minutes. 50 C.c. of standard titanous chloride (1 c.c. = 0·002679 gm. Fe) were run in and the solution was boiled over a free flame for 1 minute, while a current of carbon dioxide was passed through the flask. The excess of titanous chloride was ascertained by titration with standard crystal-scarlet solution and amounted to 33·1 c.c. Therefore 16·9 c.c. of titanous chloride were used for the reduction of the osazone, and as 180 glucose = 336 Fe, the result is equal to 99·71 per cent.

*Lævulose.* 0·05325 Gm. of pure lævulose, titrated as above, required 28·4 c.c. of titanous chloride (of which 1 c.c. = 0·003498 gm. Fe). This gives 99·8 per cent.

*Sucrose.* 4·9180 Gms. of pure sucrose were dissolved in water, the solution was made up to 50 c.c. and inverted by heating on a water-bath with 5 c.c. of concentrated hydrochloric acid for 10 minutes. The solution was made up to 500 c.c. and of this 25 c.c. were diluted to 250 c.c. Of this solution, 25 c.c. were treated (after neutralising with $N$/10-sodium carbonate) as described for glucose. The amount of titanous chloride required in the reduction was 20·7 c.c. (1 c.c. = 0·002325 gm. Fe), which represents a purity of 99·6 per cent.

*Maltose.* 0·4084 Gm. of pure maltose was dissolved in water and the solution made up to 100 c.c. Of this solution, 10 c.c. required 16·4 c.c. of titanous chloride (1 c.c. = 0·002325 gm. Fe). Purity 100·03 per cent. $C_{12}H_{22}O_{11},H_2O$. After inversion with hydrochloric acid, 0·02518 gm. required 11·7 c.c. of titanous chloride (1 c.c. = 0·004012 gm. Fe), which gives 99·8 per cent.

*Lactose.* 0·3936 Gm. was dissolved in water and made up to 100 c.c. Of this, 10 c.c. required 15·8 c.c of titanous chloride (1 c.c. = 0·002325 gm. Fe) for reduction. This result represents 99·89 per cent. $C_{12}H_{22}O_{11},H_2O$. After inversion with hydrochloric acid, 0·02510 gm. required 29·1 c.c. of titanous chloride (1 c.c. = 0·001608 gm. Fe), giving 100·2 per cent.

*Glucosamine* (chitosamine). A well-crystallised specimen of the hydrochloride was employed. It showed no loss in weight at 105° and was found to contain 16·56 per cent. Cl (calc. for $C_6H_{14}O_5NCl$, 16·48 per cent.). In the titration, 0·1105 gm. required 50·5 c.c. of titanous chloride (1 c.c. = 0·003401 gm. Fe), which shows a purity of 99·8 per cent.

It is evident that the new method is capable of wide application, not only for the quantitative estimation of the products enumerated, but more particularly of the products of hydrolysis of the more complex carbohydrates and of other substances which yield carbohydrates by hydrolysis. We are more particularly interested in the latter field and desire to reserve it for a time.

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## CCLXI.—*Resolution of* trans-cyclo*Butane*-1 : 2-*dicarboxylic Acid.*

By LEONARD JAMES GOLDSWORTHY.

THE racemic acid was prepared essentially by Perkin's method (J., 1894, **65**, 572). The crude ethyl butanetetracarboxylate was repeatedly fractionally distilled in a vacuum (compare Lean and Lees, J., 1897, **71**, 1062). The crude *cyclo*butanetetracarboxylic acid was heated at 170° until evolution of carbon dioxide ceased, the crude *cis*-acid so obtained was dissolved in water and boiled with animal charcoal, the filtered solution evaporated, and the residue dissolved in concentrated hydrochloric acid. When this solution was allowed to evaporate slowly over solid caustic potash in a vacuum, nearly colourless, well-defined crystals of the *cis*-acid were obtained. From these the *trans*-acid was prepared in the manner described by Perkin.

*Resolution by means of Quinine.*—Brucine effected a partial resolution only, but the acid was completely resolved by quinine. Quinine, 21 gms. (1 mol.) in a little alcohol, was added to *trans-cyclo*butane-1 : 2-dicarboxylic acid, 9 gms. (1 mol.) in 300 c.c. of water, the alcohol was evaporated, and the quinine salt dissolved by addition of boiling water. On cooling, the filtered solution deposited needles of the quinine salt of the *l*-acid ($[\alpha]_D$ in alcohol −193·6° after one crystallisation, and −192·9° after five crystallisations, from water and drying at 120°). 0·1508 of the salt dried at 120° gave 0·3868 $CO_2$ and 0·1020 $H_2O$; C = 70·0; H = 7·5. 0·2697 gave 18 c.c. of moist nitrogen at 762 mm. and 28°; N = 7·3. $(C_{20}H_{24}O_2N_2)_2,C_6H_8O_4$ requires C = 69·7; H = 7·1; N = 7·1 per cent. 0·0910 of the crystals, air-dried at the ordinary temperature, lost 0·0140 at 120°; $H_2O$ = 15·4.

$(C_{20}H_{24}O_2N_2)_2,C_6H_8O_4,8H_2O$

requires $H_2O$ = 15·4 per cent.

The l-*acid*, magnificent, colourless needles, m. p. 105°, from

hydrochloric acid, was prepared by decomposing the hot aqueous solution of the quinine salt by addition of ammonia, the quinine removed by filtration, and the acidified filtrate evaporated to dryness; the acid was extracted from the residue with ether. Rotation: $\alpha$ $-2\cdot10°$ in water ($c = 0\cdot8452$, $l = 2$), whence $[\alpha]_D^{20°}$ $-124\cdot3°$.

The d-*acid*, similarly isolated from the mother-liquor from the first crystallisation of the *l*-salt, separated from hydrochloric acid in crystals, m. p. 105°. 0·1094 neutralised 0·0611 NaOH [calc. for $C_4H_6(CO_2H)_2$, 0·0608]. Rotation: $\alpha + 3\cdot01°$ in water ($c = 1\cdot2208$, $l = 2$), whence $[\alpha]_D^{20°}$ $+123\cdot3°$. The *ethyl* ester, b. p. 236°/761 mm., was prepared from the *d*-acid and boiling 10 per cent. alcoholic sulphuric acid (7 parts). $\alpha + 2\cdot70°$ in acetone ($c = 1\cdot732$, $l = 2$), whence $[\alpha]_D^{20°}$ $+77\cdot9°$.

The rotation of *cyclo*butane-1 : 2-dicarboxylic acid is higher than that of the corresponding *cyclo*propane-, *cyclo*pentane-, or *cyclo*hexane-dicarboxylic acid (Goldsworthy and Perkin, J., 1914, **105**, 2641).

UNIVERSITY COLLEGE, RANGOON. [*Received, April 10th*, 1924.]

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# CCLXII.—*Derivatives of Methylstannonic Acid. Part II.*

By HERBERT LAMBOURNE.

As a result of a further study of the acyl derivatives of methylstannonic acid, seven new compounds have been prepared, some of which resemble very closely those previously described (J., 1922, **121**, 2533); their existence furnishes additional evidence for the view that methylstannonic acid has not the simple structure represented by $CH_3{\cdot}SnO{\cdot}OH$.

By the direct action of dichloroacetic, propionic, butyric, and *iso*butyric acids, respectively, on methylstannonic acid, penta-acyl derivatives of the type previously described were obtained.

$$SnMe(O{\cdot}COR)_2{\cdot}O{\cdot}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR)_2,$$

where R = $CHCl_2$ (I), $CH_3{\cdot}CH_2$ (II), $CH_3{\cdot}CH_2{\cdot}CH_2$ (III), $(CH_3)_2CH$ (IV).

Compounds II, III, and IV, on partial hydrolysis, yielded, not tri-acyl compounds (*loc. cit.*), but hexa-acyl derivatives, $(SnMeO{\cdot}O{\cdot}COR)_6$. These might have been produced by simultaneous hydrolysis and condensation of two molecules of the penta-acyl derivatives,

$$2(SnMe)_3O_2(O{\cdot}COR)_5 + 2H_2O = (SnMe{\cdot}O{\cdot}O{\cdot}COR)_6 + 4RCO_2H.$$

The same hexa-acyl compounds, however, were obtained by treat-

ing a solution of methylstannonic acid or the penta-acyl compound in the corresponding organic acid with alcohol. It is therefore assumed that methylstannonic acid, which is probably of cyclic structure, $(SnMeO{\cdot}OH)_3$, or even $(SnMeO{\cdot}OH)_6$, first dissolves in the organic acid with rupture of the closed chain, and in the solution there exists the ortho-derivative, $SnMe(O{\cdot}COR)_3$, which, however, is too unstable to be isolated. In presence of excess of the solvent (organic acid) the penta-acyl derivative can be obtained through condensation of three molecules of the ortho-compound. Addition of excess of alcohol, however, to this solution brings about hydrolysis and condensation of six molecules, yielding the more stable hexa-acyl compound :

$$6SnMe(O{\cdot}COR)_3 + 6H_2O = 12RCO_2H + O\langle\begin{matrix}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR)\\ SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR){\cdot}O{\cdot}SnMe(O{\cdot}COR)\end{matrix}\rangle O.$$

The existence of organic compounds of tin containing a closed chain of six tin and six oxygen atoms linked alternately is of considerable theoretical interest. There is a certain analogy between silicon and tin in regard to their organic and inorganic compounds. The probability of the presence in complex silicates and alumino-silicates of closed chains containing five and six atoms of silicon linked with oxygen atoms has been shown by W. and D. Asch ("Die Silicate," 1911), whilst, in connexion with organic silicon compounds, Kipping (J., 1912, **101**, 2127) has shown that in the "multi-molecular silicones," four silicon and oxygen atoms similarly linked is the maximum number yet obtained in a pure compound. The existence of the hexa-acyl tin compounds containing a closed chain of six tin and six oxygen atoms would indicate that tin exhibits possibly an even greater tendency than silicon to form such structures.

## Experimental.

*Penta-acyl Derivatives.*—The penta-acyl derivatives were prepared by adding small amounts of methylstannonic acid to the boiling acids. The *propionyl* (II), *butyryl* (III), and iso*butyryl* (IV) compounds crystallised on cooling; the *dichloroacetyl* compound (I) was extracted from the cooled melt with benzene. The products were filtered rapidly and dried in a vacuum desiccator over caustic soda.

The compounds were hydrolysed by water or ethyl alcohol; even spontaneous evaporation of a solution of the penta-*iso*butyryl compound (IV) in benzene caused partial hydrolysis, the residue consisting of a mixture of the penta-acyl and hexa-acyl compounds, which could be easily separated mechanically.

The *pentadichloroacetyl compound* (I), rhomboidal plates, m. p.

about 235—240° (decomp.), is soluble in hot benzene and in hot alcohol (Found: Sn = 33·53, 33·38; Cl = 33·11, 33·19; *M* in freezing camphor = 1092. $C_{13}H_{14}O_{12}Cl_{10}Sn_3$ requires Sn = 33·24; Cl = 33·05 per cent.; *M* = 1074).

The *pentapropionyl compound* (II), hexagonal plates, is soluble in cold benzene and in hot alcohol. It melts at 156—157°, solidifies again at 160°, and remelts at about 240° [Found: Sn = 44·66; $C_2H_5$·CO (Perkin's method) = 35·49; *M* in freezing benzene = 797. $C_{18}H_{34}O_{12}Sn_3$ requires Sn = 44·69; $C_2H_5$·CO = 35·67 per cent.; *M* = 799].

The *pentabutyryl compound* (III), m. p. 105°, is very soluble in cold benzene, ether, chloroform, and in hot alcohol (Found: Sn = 41·44; *M* in freezing benzene = 894. $C_{20}H_{44}O_{12}Sn_3$ requires Sn = 41·09 per cent.; *M* = 869).

The *pentaisobutyryl compound* (IV), rectangular prisms, m. p. 194°, is soluble in cold benzene, ether, chloroform, and in hot alcohol (Found: Sn = 41·02; *M* in freezing benzene = 830. $C_{23}H_{44}O_{12}Sn_3$ requires Sn = 41·02 per cent.; *M* = 869).

*Hexa-acyl Derivatives* (containing 6 atoms of tin).—The penta-acyl derivatives were hydrolysed, preferably with alcohol, as water tended to produce methylstannonic acid.

Compounds V and VI were obtained by boiling solutions of the corresponding penta-acyl compounds in propionic and butyric acids, respectively, with excess of alcohol. The hexa*iso*butyryl compound (VII) was prepared from the solid penta*iso*butyryl compound and boiling alcohol.

The *hexapropionyl compound* (V), rhomboidal crystals, partly melting at about 246° (decomp.), is very soluble in cold benzene, and slightly soluble in boiling acetone or alcohol. Complete hydrolysis into methylstannonic acid occurs on repeated boiling with alcohol (Found: Sn = 53·22; $C_2H_5$·CO = 25·5; *M* in freezing benzene = 1290. $C_{24}H_{48}O_{12}Sn_6$ requires Sn = 53·35; $C_2H_5$·CO = 25·57 per cent.; *M* = 1338).

The *hexabutyryl compound* (VI), rhomboidal crystals, m. p. 180°, is very soluble in cold benzene (Found: Sn = 50·24; *M* in freezing benzene = 1400. $C_{30}H_{60}O_{18}Sn_6$ requires Sn = 50·21 per cent.; *M* = 1422).

The *hexaisobutyryl compound* (VII), cubical plates, m. p. about 260°, is soluble in cold benzene, ether, chloroform, and sparingly soluble in hot alcohol (Found: Sn = 50·16; *M* in freezing benzene = 1430. $C_{30}H_{60}O_{18}Sn_6$ requires Sn = 50·21 per cent.; *M* = 1422).

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# CCLXIII.—*The Apparent Concentration of the Hydrogen-ion in Solutions Containing Sucrose.*

By THOMAS WESTON JOHNS TAYLOR and RAYMOND FRANCIS BOMFORD.

DURING recent years several investigators have determined, by the hydrogen electrode method, the apparent concentration of the hydrogen-ion in solutions of sucrose which is undergoing inversion by an acid, sometimes in the presence of a neutral salt. Jones and Lewis (J., 1920, **117**, 1120), Fales and Morrell (*J. Amer. Chem. Soc.*, 1922, **44**, 2071), and Lewis and Moran (*Trans. Faraday Soc.*, 1923, **17**, 382) found no change in the electromotive force as the inversion proceeds, and this result was accepted by Scatchard (*J. Amer. Chem. Soc.*, 1923, **45**, 1580). The object of the present paper is to show that the *E.M.F.* slowly drops to a constant value, which is about 1 per cent. smaller than the initial value in the cells used, and that therefore the apparent hydrogen-ion concentration increases by about 7 per cent. during the inversion.

The solutions, which were prepared in a thermostat, contained 10 gms. of ash-free commercial sucrose in 100 c.c., and were uniformly decinormal in hydrochloric acid, the acid coming from a stock solution standardised by two methods. Carefully purified alkali chlorides were used, and commercial hydrogen, which was washed with alkaline permanganate and *N*/10-hydrochloric acid. The experiments were all made at 25°, with a decinormal calomel electrode and a bridge of saturated potassium chloride solution. The *E.M.F.*'s were measured on a potentiometer of 5028 ohms resistance, using two cadmium cells independently made up and concordant; the whole apparatus was insulated on paraffin wax or ebonite. All electrode vessels had reservoirs from which the tube connecting the electrode to the bridge solution could be washed with the electrode liquid. Diffusion of potassium chloride from the bridge into the electrode liquids was guarded against by immersing the electrodes in the bridge for the minimum time and washing out the connecting tubes. That the precautions were sufficient was proved for the calomel electrode by using it at frequent intervals to complete the cell

$$Hg|Hg_2Cl_2|N/10\text{-}KCl|KCl\ sat.|N/10\text{-}HCl|H_2(760\ mm.)\ Pt:$$

the *E.M.F.* of this was found to be 0·4000 to 0·4002 volt; Loomis and Acree (*Amer. Chem. J.*, 1911, **46**, 632) found 0·4001, and Harned (*J. Amer. Chem. Soc.*, 1915, **37**, 2460) found 0·4004. For the hydrogen electrode, the absence of diffusion was shown by analysing the electrode liquid for total chloride after a series of readings, and

also by using solutions which had been kept in sealed glass vessels and not in the cells. The concordance of the readings from these solutions with the others also shows that the observed decreases are not caused by evaporation or any other effect arising from the current of hydrogen.

The following results were obtained at 25°; the experimental error is estimated at 1 in 1000; no correction for atmospheric pressure has been applied, this could not exceed 0·0003 volt in the maximum cases. By "Time" is meant the time after making up the solution.

| | | | | | |
|---|---|---|---|---|---|
| I. | Time (hours) ..... | 1 | 2 | 3 | 26 |
| $x = 0$. | *E.M.F.* (int. volt) | 0·3962 | 0·3957 | 0·3961 | 0·3936 |
| I. | Time (hours) ..... | 29 | 101 | infinity | |
| $x = 0$. | *E.M.F.* (int. volt) | 0·3937 | 0·3927 | 0·3929 | |
| II. | Time (hours) ..... | 1 | 1 | 1·5 | 7·5 |
| $x = 0{\cdot}5$. | *E.M.F.* (int. volt) | 0·3911 | 0·3915 | 0·3910 | 0·3899 |
| II. | Time (hours) ..... | 19 | 22 | 66 | 70 |
| $x = 0{\cdot}5$. | *E.M.F.* (int. volt) | 0·3899 | 0·3895 | 0·3888 | 0·3888 |
| II. | Time (hours) ..... | 97 | | infinity | |
| $x = 0{\cdot}5$. | *E.M.F.* (int. volt) | 0·3884 | 0·3882 | 0·3882 | 0·3879 |
| III. | Time (hours) ..... | 1 | 3 | 3·5 | 19 |
| $x = 1{\cdot}0$. | *E.M.F.* (int. volt) | 0·3864 | 0·3857 | 0·3853 | 0·3834 |
| III. | Time (hours) ..... | 20·5 | 50 | 66·5 | |
| $x = 1{\cdot}0$. | *E.M.F.* (int. volt) | 0·3836 | 0·3827 | 0·3822 | |

($x$ = Concentration of sodium chloride.)

The drop in *E.M.F.* would appear to be associated with the inversion of the sucrose; for sodium chloride, which accelerates inversion, causes a more rapid drop in *E.M.F.* when in normal solution; but the effect is small at $N/2$. Jones and Lewis have shown that increase of sucrose concentration increases the apparent hydrogen-ion concentration and the effect described here is probably analogous to this; but since the experimental error is about 8 per cent. of the observed drop in *E.M.F.*, any theoretical deductions are untrustworthy.

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# CCLXIV.—*The Explosion of Ammonia with Electrolytic Gas and Oxygen.*

By James Riddick Partington and Alfred John Prince.

The explosive properties of mixtures of ammonia and oxygen were studied by Fourcroy ("Philosophie chimique," 1806, p. 229; "Système des connaissances chimique," An IX, vol. 2, p. 236) and much more thoroughly by Henry (*Phil. Trans.*, 1809, **99**, 430; Gilbert's *Annalen*, 1810, **36**, 291). With the exception of some experiments on the action of the silent discharge on the mixture (Mixter, *Amer. J. Sci.*, 1898, [iv], **6**, 217; Besson, *Compt. rend.*, 1911, **152**, 1850), and a communication in an obscure journal which was not available to us until the work was completed (Neumann, *Math. es Termes. Eresto.*, 1889, **6**, 54; the results were in general agreement with those of Henry), no more recent investigations are known to us. Henry's conclusions were that (i) with excess of oxygen, although all the ammonia disappeared and the residue contained nitrogen with excess of oxygen, yet ammonium nitrate was formed; (ii) with excess of ammonia, no ammonium nitrate was formed, but the ammonia "was completely decomposed. Part of its hydrogen is sufficient for the saturation of the oxygen and the remaining hydrogen and the whole of the nitrogen of the ammonia remain in a gaseous state"; (iii) when the proportions of ammonia to oxygen were greater than 3 to 1, or less than 1·4 to 1, the mixture ceased to be inflammable.

In the present investigation, pure dry ammonia was exploded with pure dry electrolytic gas ($2H_2 + O_2$) or oxygen in a vessel of definite shape and capacity, at a definite initial temperature and pressure, such that all the steam formed remained gaseous.

The principal drying agent for the electrolytic gas and oxygen was purified phosphoric oxide. Threlfall (*Phil. Mag.*, 1893, [v], **35**, 14) and Shenstone and Beck (J., 1893, **63**, 475) distilled the commercial product in oxygen over platinum; Baker (Finch and Peto, J, 1922, **121**, 695), finds platinum unnecessary, and our experiments agree with Baker's result.

We at first used Chapman's method (J., 1911, **99**, 1871). The product was quite pure, but was frequently obtained in lumps instead of powder, and the burning of the phosphorus had to be most carefully controlled, otherwise lower oxides were produced. Fairly good yields were obtained by the following method. A tube of Kavalier glass, about 4 feet in length and 1 inch in diameter, was heated to dull redness, a current of dry air being aspirated through it. Commercial phosphoric oxide was then *rapidly* introduced at

one end and heated, when it readily volatilised. The vapour passed with the air through the hot tube and was condensed as a powder in a cool receiver. The product had no action on silver nitrate or mercuric chloride. The tube could be used about four times and then cracked (Finch and Peto, *loc. cit.*, recommend an iron tube, which would probably be more convenient; the paper appeared too late for us to test the method).

Electrolytic gas leaving no residue on sparking was produced by the electrolysis of a hot solution of recrystallised barium hydroxide, with nickel electrodes (Baker, J., 1902, **81**, 400; Park and Partington, this vol., 72) and dried over pure calcium chloride and phosphoric oxide.

Ammonia was prepared by the decomposition by heat of a mixture of ammonium chloride, purified according to the method of Stas ("Recherches sur les rapports réciproques des poids atomiques," 1860, p. 82; "Nouvelles recherches sur les lois des proportions chimiques," 1865, p. 48), with partly slaked pure lime (Guye and Pintza, *Mem. Soc. Phys. Nat. Geneve*, 1908, **35**, 594). The mixture was contained in a glass tube connected with a manometer and purifying train consisting of two tubes of quicklime and one tube of broken caustic soda. The gas was completely absorbed by cold, recently boiled water.

The oxygen, obtained by heating pure mercuric oxide in hard glass, was passed over broken stick caustic soda to remove traces of oxides of nitrogen, dried by pure calcium chloride, and purified phosphoric oxide, and was completely absorbed by an alkaline solution of sodium hyposulphite ($Na_2S_2O_4$).

The explosion apparatus consisted of a spherical Duroglass bulb of exactly 100 c.c. capacity between the mark on the capillary stem and the accurate stopcock, held in place by strong springs. The bulb was fitted with platinum firing wires, prolonged by glass ears and glass tubes fitting into short tubulures on the bulb (sealed off from the inside of the latter) by rubber stoppers. The bulb was mounted inside a cubical copper water-bath provided with a stirrer and an accurate thermometer, and plate glass windows were cemented in by a mixture of litharge and plaster of Paris. The requisite volumes of the gases were passed into the bulb from a carefully calibrated burette of a Macfarlane and Caldwell gas analysis apparatus. The mercury used in the apparatus was frequently purified and was dried after each experiment by heating; the glass explosion bulb and gas burette were also carefully cleaned and dried after each experiment. These precautions, and complete absence of moisture (as pointed out by Henry) are absolutely essential. When the mixture had attained the temperature of the bath, it was fired by a spark.

In all the experiments the gas was at 85° and under a pressure of 380 mm. of mercury when the explosion occurred, and all the steam remained in the gaseous state during and after the explosion. The volumes of gas initially taken were such that they just filled the 100 c.c. bulb at 85° and 380 mm.

The cooled gas was passed after the explosion into the measuring burette and was, in the first series of experiments, a mixture of nitrogen and hydrogen. It was analysed by a modification of a method also suggested by Henry (*Ann. Phil.*, 1825, **25**, 424), *viz.*, the catalytic combustion of the hydrogen after the addition of oxygen, on a roll of palladium foil in a fused quartz tube. Pure oxygen was prepared by the electrolysis of barium hydroxide solution in a divided cell, passed over heated platinised asbestos, and dried as before. A suitable quantity was added to the gas in the burette, and the mixture passed backwards and forwards over the palladium in the silica tube heated at about 200°. The excess of oxygen was removed with alkaline pyrogallol and the residual nitrogen measured. A correction was applied for the volume of air in the silica capillary, since the palladium could not be brought in contact with mercury. The palladium must not be allowed to glow, otherwise oxides of nitrogen are produced and explosions may occur.

In the explosions with electrolytic gas, various mixtures were made up as shown in Table I. The volume of gas filling the bulb at 85° and 380 mm. is 38·13 c.c. at *S.T.P.*, but a correction of 1·5 per cent. was made on the volume of ammonia measured at room temperature on account of the deviation from Boyle's law (compressibility coefficient = 0·01504, Leduc, *Ann. Chim. Phys.*, 1910, [viii], **19**, 441; ideal gas volume of ammonia = measured volume × 1·015). The figures in the table refer to the *ideal* volumes of ammonia, and all volumes are calculated for the dry gases reduced to *S.T.P.*

The effect of increasing the ratio of electrolytic gas to ammonia, *i. e.*, of raising the temperature of explosion, on the decomposition is seen in Table II. The decomposition with the lowest ratio which is inflammable is nearly 80 per cent. With an increasing ratio, the decomposition increases steadily until with a ratio of a little more than 3 volumes of electrolytic gas to 1 volume of ammonia the decomposition of the latter is complete. The decomposition remains complete when the ratio is increased to 5 volumes to 1 volume, and there is no sign of a reversal at higher temperatures.

The explosion of ammonia with oxygen was carried out in the same way as with electrolytic gas. In the experiments with a deficiency of oxygen, the gases again consisted of nitrogen and

TABLE I.

Ammonia Exploded with Electrolytic Gas.

| C.c. of ammonia. | C.c. of electrolytic gas. | Ratio electr. gas/$NH_3$. | Residual vol. | Vol. after $O_2$ added. | Vol. after Pd. | C.c. of $H_2$. | C.c. of $N_2$. |
|---|---|---|---|---|---|---|---|
| 22·12 | 16·34 | 0·76 | Mixture will not explode. | | | | |
| 20·63 | 17·80 | 0·89 | ,, | ,, | ,, | | |
| 19·84 | 18·58 | 0·96 | ,, | ,, | ,, | | |
| 19·34 | 19·06 | 1·01 | 30·55 | 46·72 | 12·43 | 22·86 | 7·69 |
| 18·88 | 19·53 | 1·06 | 32·44 | 45·17 | 8·72 | 24·30 | 8·14 |
| 17·54 | 20·84 | 1·22 | 31·84 | 48·01 | 12·13 | 23·92 | 7·92 |
| 15·89 | 22·57 | 1·46 | 29·13 | 41·35 | 8·61 | 21·83 | 7·30 |
| 15·16 | 23·19 | 1·57 | 28·34 | 42·18 | 10·32 | 21·24 | 7·10 |
| 13·93 | 24·40 | 1·81 | 26·50 | 39·56 | 9·83 | 19·82 | 6·68 |
| 13·62 | 24·70 | 1·87 | 26·02 | 38·62 | 9·40 | 19·48 | 6·56 |
| 13·34 | 24·98 | 1·93 | 25·54 | 35·39 | 6·55 | 19·23 | 6·31 |
| 12·89 | 25·42 | 2·03 | 25·10 | 34·83 | 6·59 | 18·82 | 6·28 |
| 12·72 | 25·59 | 2·07 | 24·98 | 38·05 | 9·97 | 18·72 | 6·26 |
| 12·25 | 26·06 | 2·19 | 24·41 | 37·37 | 9·88 | 18·33 | 6·08 |
| 9·67 | 28·62 | 3·04 | 19·37 | 28·21 | 6·37 | 14·56 | 4·81 |
| 7·74 | 30·50 | 4·06 | 15·50 | 26·88 | 9·49 | 11·59 | 3·91 |
| 6·44 | 31·78 | 5·07 | 12·90 | 20·23 | 5·74 | 9·66 | 3·24 |

TABLE II.

Amount of Decomposition with Varying Ratios of Electrolytic Gas to Ammonia.

$a$ = Ratio of electrolytic gas to ammonia. $b$ = Percentage decomposition of ammonia.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $a$ ..... | 1·01 | 1·06 | 1·22 | 1·46 | 1·57 | 1·81 | 1·87 |
| $b$ ..... | 79·0 | 86·0 | 90·4 | 91·7 | 93·6 | 95·15 | 95·55 |
| $a$ ..... | 1·93 | 2·03 | 2·07 | 2·19 | 3·04 | 4·06 | 5·07 |
| $b$ ..... | 95·8 | 97·3 | 98·2 | 99·4 | 100 | 100 | 100 |

hydrogen, and were analysed as before. The results obtained by exploding with a deficiency of oxygen, with the 100 c.c. explosion bulb filled at 85° and 380 mm. pressure, are given in Table III. As before, all volumes refer to dry gases at *S.T.P.*

TABLE III.

Explosion of Ammonia with Oxygen.

| C.c. of ammonia (ideal). | C.c. of oxygen. | Ratio $NH_3/O_2$. | C.c. of residual gas. | C.c. of $H_2$. | C.c. of $N_2$. |
|---|---|---|---|---|---|
| 30·95 | 7·63 | 4·06 | Burnt only in track of the spark. | | |
| 29·05 | 9·53 | 3·04 | ,, | ,, | ,, |
| 28·59 | 9·96 | 2·83 | 37·31 | 22·90 | 14·41 |
| 27·95 | 10·59 | 2·64 | 34·95 | 20·90 | 14·05 |
| 27·32 | 11·21 | 2·43 | 31·60 | 18·03 | 13·57 |
| 26·61 | 11·91 | 2·23 | 29·62 | 16·25 | 13·37 |
| 25·81 | 12·70 | 2·03 | 25·98 | 13·23 | 12·75 |
| 23·81 | 14·67 | 1·61 | 17·96 | 6·08 | 11·88 |
| 22·57 | 15·89 | 1·41 | 14·63 | 2·36 | 12·27 |
| 22·03 | 16·41 | 1·34 | 12·01 | 1·01 | 11·00 |

The results confirm generally those found by Henry, *viz.*, that when ammonia is fired with a deficiency of oxygen, the excess of ammonia is completely decomposed into nitrogen and hydrogen, although mixtures with a lower ratio $NH_3/O_2$ than 1·4 (Henry's limiting ratio) were still explosive. In Table IV, the volumes of nitrogen and hydrogen produced are compared with those required by this hypothesis.

TABLE IV.

Ammonia Exploded with Deficiency of Oxygen.

| Ratio $NH_3/O_2$. | Volumes of gas obtained. | | Volumes of gas calculated. | |
|---|---|---|---|---|
| | Hydrogen. | Nitrogen. | Hydrogen. | Nitrogen. |
| 2·83 | 22·90 | 14·41 | 22·97 | 14·30 |
| 2·64 | 20·90 | 14·05 | 20·73 | 13·97 |
| 2·43 | 18·03 | 13·57 | 18·53 | 13·65 |
| 2·23 | 16·25 | 13·37 | 16·08 | 13·30 |
| 2·03 | 13·23 | 12·75 | 13·31 | 12·90 |
| 1·61 | 6·08 | 11·88 | 6·36 | 11·90 |
| 1·41 | 2·36 | 12·27 | 2·06 | 11·28 |
| 1·34 | 1·01 | 11·00 | 0·22 | 11·01 |

The reaction which occurs when ammonia is exploded with half its volume of oxygen may be represented, for example, by the equation $2NH_3 + O_2 = N_2 + H_2 + 2H_2O$. The hydrogen values for the mixtures having the ratios 1·41 and 1·34 in Tables III and IV are higher than those required by the above theory. In these mixtures, a small part of the oxygen in all probability reacted with the nitrogen, since the preferential burning of the hydrogen will not be quantitative in any case, and the less so as the higher oxygen ratios are approached. The high nitrogen residues in these two explosions, particularly in the former, are probably due to errors of experiment. With fairly high oxygen ratios, it appears that some nitrogen is burnt even with a deficiency of oxygen. In no case was any residue of ammonia detectable by Nessler's reagent found in the washings of the bulb after the explosion. Henry and Mixter (*loc cit.*) both report the formation of ammonium nitrate and nitrite on the explosion or reaction of certain mixtures. No trace of ammonia was found in the residues after the explosion of mixtures containing an excess of oxygen, to the consideration of which we now turn. We may remark that when these mixtures are exploded in narrow tubes open at one end, by the application of a flame, a distinct cloud of ammonium nitrate is seen at the closed end of the tube after the explosion. It is possible that this is produced when the gases are fired at atmospheric pressure, and further investigations are to be made to decide this point.

In the mixtures with excess of oxygen, oxides of nitrogen are

produced, in some cases, as will be seen later, in considerable amounts. These were estimated by passing the residual gas, immediately after the explosion, into a second gas burette containing mercury covered with a layer of caustic soda solution. To this liquid were added the washings of the explosion bulb, and the "fixed nitrogen" in the liquid was determined by reduction with Devarda's alloy and distillation. Its volume in c.c. is given in Table V.

TABLE V.

Explosion of Ammonia with excess of Oxygen.

| Vol. of $NH_3$ (ideal). | Vol. of $O_2$. | Ratio $O_2/NH_3$. | Residual vol. | Vol. of $N_2$. | Vol. of excess $O_2$. | Fixed N. | Per cent. N oxidised. | Colour of flame. |
|---|---|---|---|---|---|---|---|---|
| 20·84 | 17·53 | 0·84 | 12·10 | 10·39 | 1·71 | — | — | Yellow |
| 19·28 | 19·04 | 0·99 | 14·30 | 9·33 | 4·97 | 0·45 | 4·7 | ,, |
| 17·29 | 21·09 | 1·22 | 14·24 | 7·26 | 6·98 | 1·4 | 16·2 | Greenish-yellow. |
| 16·47 | 22·88 | 1·48 | 16·94 | 6·94 | 10·00 | 1·2 | 15·6 | Lilac |
| 12·89 | 25·42 | 1·97 | 20·04 | 5·59 | 14·45 | 0·95 | 15·0 | White |
| 11·04 | 27·24 | 2·47 | 22·48 | 4·72 | 17·76 | 0·8 | 14·5 | ,, |
| 9·66 | 28·60 | 2·96 | 24·65 | 4·20 | 20·45 | 0·7 | 14·5 | ,, |
| 8·59 | 29·66 | 3·45 | 26·30 | 3·84 | 22·46 | 0·5 | 11·6 | ,, |
| 8·16 | 30·09 | 3·69 | 26·71 | — | — | — | — | |
| 7·74 | 30·50 | 3·94 | Mixture could not be exploded. | | | | | |
| 6·93 | 31·40 | 4·53 | ,, | ,, | ,, | | | |
| 6·35 | 31·78 | 5·00 | ,, | ,, | ,, | | | |

The colour of the flame in the explosion varied in a striking manner with the proportions of combustible gas to oxygen, as is seen in the table. Some experiments were made on the spectra of the flames, and our further experiments in this directon may throw some light on the mechanism of the reaction.

The maximum proportion of ammonia oxidised in these experiments is about 16 per cent. This appears to fall off with ratios of oxygen to ammonia greater than 1·2, but not to a marked extent until the mixture approaches the non-inflammable limiting ratio 3·9. The high oxidation is accompanied by a change in the appearance of the flame.

On the assumption that ammonia, in its reaction with oxygen, first undergoes practically complete dissociation, one would expect that an equivalent mixture of nitrogen and hydrogen would behave similarly towards oxygen. The experiments recorded in Table V were therefore repeated with equivalent amounts of hydrogen and nitrogen in place of the ammonia.

Since ammonia occupies a smaller volume than its constituent elements, smaller amounts of the latter had to be taken to fill the bulb at 85° and 380 mm. The numerical ratios were then multiplied by a factor to reduce them to an exact parallel with the ammonia–

oxygen explosion experiments. The results are shown in Table VI. The numbers in the first column give the actual ratios $O_2/NH_3$, those in the second column twice the actual ratios $O_2$/(mixture $N_2 + 3H_2$).

TABLE VI.

Explosion of Nitrogen and Hydrogen Mixtures with Oxygen.

| Ratio $O_2/NH_3$ with $NH_3$. | Ratio $O_2$/ equiv. $NH_3$ with mixture. | Residual vol. (c.c.). | | C.c. of $N_2$. | | C.c. of $O_2$. | |
|---|---|---|---|---|---|---|---|
| | | $NH_3$. | Mixture. | $NH_3$. | Mixture. | $NH_3$. | Mixture. |
| 0·99 | 0·99 | 14·30 | 14·50 | 9·33 | 9·52 | 4·97 | 4·92 |
| 1·22 | 1·22 | 14·24 | 14·34 | 7·26 | 7·44 | 6·98 | 6·90 |
| 1·48 | 1·48 | 16·94 | 17·29 | 6·94 | 6·87 | 10·00 | 10·42 |

From the results, the volume of fixed nitrogen for three ratios of oxygen to ammonia or equivalent of nitrogen and hydrogen mixture, in the initial mixture, were found to be :

| | Nitrogen oxidised. | |
|---|---|---|
| Ratio $O_2/NH_3$. | With ammonia. | With mixture. |
| 0·99 | 0·46 c.c. | 0·24 c.c. |
| 1·22 | 1·40 ,, | 1·15 ,, |
| 1·48 | 1·20 ,, | 1·00 ,, |

The proportion of nitrogen oxidised is slightly higher in all cases when ammonia is exploded than when a mixture of nitrogen and hydrogen, such as would have been derived from this ammonia by complete decomposition, is substituted.

The effect of firing ammonia and the equivalent mixture with a mixture of carbon monoxide and oxygen is engaging our attention. The results will have a bearing on the radiation theory of chemical action which is obvious.

*Summary.*

(1) Mixtures of ammonia with electrolytic gas ($2H_2 + O_2$) in varying proportions were exploded with the mixture initially at 85° and under a pressure of 380 mm. so that no steam could condense. The mixture became explosive with a ratio of electrolytic gas to ammonia just above 1, when 79 per cent. of the ammonia was decomposed. When the ratio was just above 3, the decomposition was complete. No reversal of the proportion of decomposition was found with still higher ratios.

(2) Mixtures of ammonia and oxygen were exploded under the same conditions. With ratios of ammonia to oxygen greater than 1·6 the oxygen unites preferentially with the hydrogen of the ammonia, leaving a residue of nitrogen and excess of hydrogen unburnt. When this ratio falls below 1·6, oxides of nitrogen are formed, the maximum oxidation of nitrogen being 16 per cent. with the ratio 1·22.

(3) When mixtures of nitrogen and hydrogen are exploded with oxygen, the amount of nitrogen oxidised is less than when the ammonia which would be formed from these mixtures is exploded with the same ratio of oxygen.

(4) The commencement of oxidation of nitrogen in (2) is accompanied by a definite change in the appearance of the flame.

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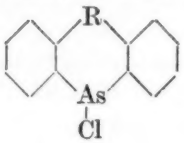
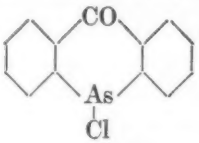
## CCLXV.—*Organic Compounds of Arsenic. Part I. Derivatives of* o-*Benzarsinic Acid.*

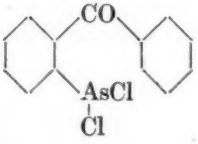
By JOHN ALFRED AESCHLIMANN and NIAL PATRICK MCCLELAND.

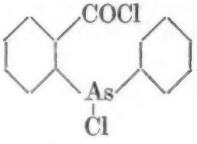
COMPOUNDS of the type (I) are known in which R is NH (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1; Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218), or O (Lewis, Lowry, and Bergeim, *ibid.*, p. 890), or AsCl (Kalb, *Annalen*, 1921, **423**, 39).

(I.) 

(II.)

(III.) 

(IV.)

The object of the present research was to prepare a compound of the structure (II) analogous to acridone. This compound should be obtainable from *benzophenone*-o-*dichloroarsine* (III), or from the *acid chloride* (IV) of *o*-carboxydiphenylchloroarsine, by elimination of hydrogen chloride. When the latter was treated with aluminium chloride, however, an isomeric change took place, most probably through the ring compound (II), and benzophenone-*o*-dichloroarsine (III) was formed, from which no derivative of the acridone type could be obtained.

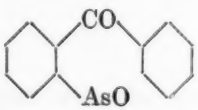
Benzophenone-*o*-dichloroarsine was prepared from anthranilic

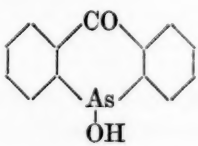
acid in accordance with the following scheme (for similar reactions in the para-series, see Fourneau and Oechslin, *Bull. Soc. chim.*, 1912, [iv], **11**, 910; Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1921, **43**, 2119); the latter authors have described the reaction for the ortho-compound, but have not isolated the dichloroarsine (*ibid.*, 1923, **45**, 510) :

$$C_6H_4\langle{}^{CO_2H}_{NH_2} \longrightarrow C_6H_4\langle{}^{CO_2H}_{AsO_3H_2} \xrightarrow[+PCl_5]{PCl_5}$$

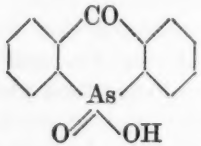
$$C_6H_4\langle{}^{COCl}_{AsCl_2} \xrightarrow[+C_6H_6]{AlCl_3} C_6H_4\langle{}^{COPh}_{AsCl_2}$$

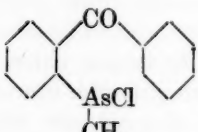
Although hydrogen chloride was evolved on heating benzophenone-*o*-dichloroarsine in a vacuum, or on continuing the condensation with aluminium chloride, the resulting gum would not distil and did not give rise to any crystalline products which could be identified as derivatives of the closed ring structure. By treatment of the gum with hydrochloric acid the original dichloroarsine was produced, and by oxidation in alkaline solution benzophenone-*o*-arsinic acid was formed. By treatment with alkali alone and subsequent acidification, an amorphous oxide was obtained which was probably benzophenone-*o*-arsenious oxide, although the identity could not be proved on account of the indefinite melting point of the oxide and the fact that it could not be obtained in a state of sufficient purity to give good analytical results. The difficulty of obtaining derivatives of benzophenone-*p*-arsenious oxide in the pure state has been observed by Lewis and Cheetham (*loc. cit.*). Another difficulty in identifying this product arises from the isomerism of benzophenone-*o*-arsenious oxide (V) with the hydroxide (VI). The latter, however, would probably exist as an oxide rather than in the hydroxide form, and, further, should give rise to an arsinic acid (VII) on oxidation, and not to benzophenone-*o*-arsinic acid.

(V.) 

(VI.)

(VII.) 

(VIII.)

Attempts have been made to form the closed ring acid (VII) by removing the elements of water from benzophenone-*o*-arsinic acid

(*o*-benzoylphenylarsinic acid) in the same way as anthraquinone is prepared from *o*-benzoylbenzoic acid. The arsinic acid remained unacted upon by cold concentrated sulphuric acid and was decomposed when warmed with this reagent; it was similarly decomposed on treatment with phosphorus pentoxide, or on heating in a vacuum above 100°. The instability of the arsinic acid group in the ortho-position to a ketone group has been observed by Benda (*J. pr. Chem.*, 1917, [ii], **95**, 84) in the case of anthraquinone-1-arsinic acid.

While dichloroarsines do not condense readily with aromatic hydrocarbons in the normal Friedel and Crafts reaction, condensation takes place between benzene and monochloroarsines (Burrows and Turner, J., 1920, **117**, 430), and it was considered probable that the same would apply to internal condensation. *Benzophenone-o-methylchloroarsine* (VIII) was accordingly prepared and the condensation attempted in various solvents, but except for a partial hydrolysis to the oxide in the subsequent treatment with water, the substance was recovered unchanged.

The o-*carboxydiphenylchloroarsine* required for the second method of synthesis was obtained from the corresponding diarylarsinic acid, which was prepared by Bart's reaction either by coupling sodium phenylarsinite with diazotised anthranilic acid, or by using sodium benzarsinite and diazotised aniline (A). The second method was preferable when it was intended to isolate the arsinic acid, but this was not usually necessary, as the impure acid obtained by the first method can be extracted with hydrochloric acid and reduced at once.

(A.) $C_6H_4\langle^{CO_2H}_{N_2Cl} + (NaO)_2AsPh \longrightarrow$

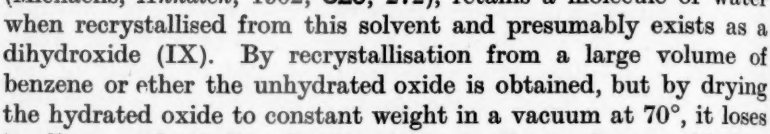
$$C_6H_4\langle^{CO_2H}_{AsPhO\cdot ONa} \longleftarrow C_6H_4\langle^{CO_2H}_{As(ONa)_2} + PhN_2Cl$$

Carboxydiphenylchloroarsine could not be dehydrated by treatment with sulphuric acid, so it was converted into the acid chloride (IV), and this was dissolved in carbon disulphide and treated with aluminium chloride. The product was decomposed with water in the usual way, but the substance isolated from the benzene extract contained a lower percentage of chlorine than was required for the closed ring ketone (II) and behaved like a mixture of benzophenone-*o*-arsenious oxide and chloride. By treatment with alkaline hydrogen peroxide, benzophenone-*o*-arsinic acid was obtained, and if hydrochloric acid had been used to decompose the aluminium chloride condensation product, benzophenone-*o*-dichloroarsine (III) crystallised out on standing. It seems probable that the reaction had taken place according to the scheme (B).

(B.) (IV.) $\xrightarrow{-HCl}$ (II.) $\xrightarrow{+HCl}$ (III.)

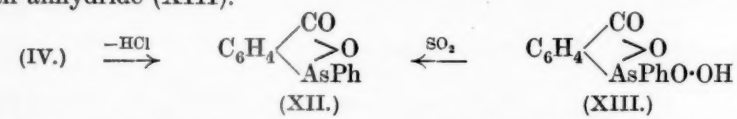
*Anhydro-derivatives from* o-*Benzarsinic Acid.**

Benzarsenious oxide, in common with other aromatic arsenious oxides having a negative substituent in the benzene nucleus (Michaelis, *Annalen*, 1902, **320**, 272), retains a molecule of water when recrystallised from this solvent and presumably exists as a dihydroxide (IX). By recrystallisation from a large volume of benzene or ether the unhydrated oxide is obtained, but by drying the hydrated oxide to constant weight in a vacuum at 70°, it loses in all one and a half molecules of water; the product would then correspond to the constitution X.




*o*-Benzarsenious chloride lost a molecule of hydrogen chloride on distillation at low pressures, and the analysis and molecular weight of the product indicated that the condensation had occurred between the carboxyl and chloroarsine groups. The product (XI) was reconverted into benzarsenious chloride when treated with hydrogen chloride in neutral solvents.

The same occurred with *o*-carboxydiphenylchloroarsine; the product of the condensation (XII) was also obtained by reduction of *o*-carboxydiphenylarsinic acid, which was itself only isolated as an anhydride (XIII).



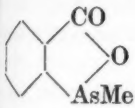

The relation between these compounds shows that the anhydride of the acid has the structure (XIII) and not (VII), from which the ketone (II) should be obtained by reduction in hydrochloric acid solution. The compound (XII) also was reconverted into *o*-carboxydiphenylchloroarsine by treatment with gaseous hydrogen chloride in neutral solvents.

*o*-Carboxyphenylmethylchloroarsine similarly loses hydrogen chloride on distillation and produces o-*carboxyphenylmethylarsinous anhydride* (XIV), which is also obtained by reduction of *o*-carboxyphenylmethylarsinic acid in aqueous solution. The latter acid itself does not possess the anhydride structure.

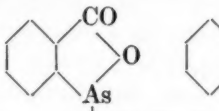
A case of particular interest is that of *oo'-dicarboxydiphenylarsinous anhydride* (XV). Here the presence of the two ortho-

* Compare Michaelis, *Annalen*, 1902, **320**, 314; **321**, 174, for trimethyl-*p*-benzarsenious betaine and similar compounds.

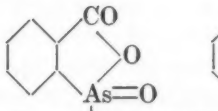
carboxyl groups, which enables the ring to be closed in two ways, causes the loss of hydrogen chloride from dicarboxydiphenylchloroarsine to be spontaneous, and the anhydride is produced whenever the chloroarsine would be expected. When this anhydride is dissolved in methyl alcohol and treated with hydrogen chloride, the *dimethyl* ester of dicarboxydiphenylchloroarsine (XVII) is produced, and when this is hydrolysed, even in acid solution, the anhydride is recovered. *oo'*-Dicarboxydiphenylarsinic acid * exists as an anhydride (XVI), and the ring is only slowly opened up by alkalis, so that it behaves as a monobasic acid on titration unless treated with excess of alkali.



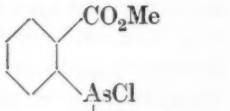

(XIV.)




(XV.)




(XVI.)




(XVII.)

The anhydride ring seems to be more readily formed the higher the molecular weight of the radical attached to the arsenic atom, as in the case of the higher derivatives even the arsinic acids exist as internal anhydrides. The ease with which these five-membered rings are formed is in marked contrast to the difficulty experienced above in obtaining the six-membered ring. The complex nature of the reaction occurring in the closing of the six-membered arsanthrene ring (Kalb, *loc. cit.*) should be noticed in this connexion. It is noteworthy that these anhydro-derivatives are the internal anhydrides of secondary hydroxyarsines, and their formation appears to be due to some tendency of the latter to exist only as anhydrides.

## Experimental.

o-*Benzarsinic acid* was prepared from anthranilic acid by Lewis and Cheetham's modification (*loc. cit.*) of Bart's method, but more concentrated solutions were employed. The yield is about equal to the weight of anthranilic acid taken. The acid does not melt below 320°; it is slightly soluble in cold water, readily in hot water or in alcohol, insoluble in ether or chloroform. It forms a salt neutral to phenolphthalein with two equivalents of alkali.

* Attempts have been made to resolve this compound, which contains an asymmetric arsenic atom, by means of its brucine and quinine salts. No definite difference was observed in the rotatory powers of various fractions of the salts and the racemic acid was recovered from them. The method of resolving compounds of the type R'R''R'''R''''As·X or R'R''R'''As:X by means of acidic or basic groups in one of the radicals R possesses obvious advantages and is being applied to other compounds.

o-*Benzarsenious oxide* was obtained by reducing benzarsinic acid in aqueous solution with sulphur dioxide and a little hydriodic acid at 60°; the crystalline oxide separated on scratching (yield 150 gms. from 140 gms. of anthranilic acid). The oxide crystallised from water melts at 89°, resolidifies at about 140°, and remelts at 225—231°. Its behaviour on recrystallisation from benzene or ether and on heating is described on p. 2028. The internal anhydride (X) melts at 231° after sintering at 225° (Found : for product from water, C = 36·3; H = 3·0. $C_7H_5O_3As,H_2O$ requires C = 36·5; H = 3·0 %. Found : for product from ether, C = 39·2; H = 2·7. $C_7H_5O_3As$ requires C = 39·6; H = 2·4 %. Found : for material dried in a vacuum, C = 41·0; H = 2·0. $C_{14}H_8O_5As_2$ requires C = 41·4; H = 2·0 %. Loss on drying = 11·8 % of weight of hydrated oxide. Calculated for $1\frac{1}{2}$ $H_2O$, 11·7 %).

On heating at 100° for 5 hours with sodium hydroxide solution (3 equivs.), the oxide was almost completely hydrolysed to benzoic acid and arsenious oxide; about 15 % was converted into monosodium dicarboxydiphenylarsinite.

o-*Benzarsenious Chloride*.—The mixture of benzarsenious oxide and chloride obtained by reducing the acid in hydrochloric acid with sulphur dioxide and a trace of an iodide was converted into the chloride by treatment with gaseous hydrogen chloride in benzene or chloroform solution.

o-*Carboxyphenylchloroarsinous Anhydride* (XI).—The anhydride, colourless crystals, m. p. 145°, which has been produced only from benzarsenious chloride by distillation in a vacuum, distils at about 220°/15 mm. The vitreous distillate slowly crystallises on standing, or on crystallising from benzene–petroleum. The distillation of the product obtained by a treatment of *o*-benzarsinic acid with phosphorus trichloride in chloroform solution, forms a convenient method of preparation of the anhydride without isolation of benzarsenious chloride. It is moderately soluble in warm benzene, chloroform or ether, readily in alcohol and in warm sodium carbonate solution (Found : C = 36·8; H = 1·76; Cl = 15·14; *M*, in freezing benzene, = 242, 243, 390, 335 with increasing concentration. $C_7H_4O_2ClAs$ requires C = 36·44; H = 1·73; Cl = 15·5 %; *M* = 230·5). It titrates with alkali as a dibasic acid (equiv. = 116), while the chloride is tribasic (equiv. = 89). After the titration with alkali, the chlorine can be determined in the same solution by the method of Volhard.

*Benzophenone-*o*-dichloroarsine* (III).—Dichloro-*o*-arsinobenzoyl chloride (30 gms. of the undistillable oil obtained from *o*-benzarsinic acid by Lewis and Cheetham's method, *loc. cit.*) and dry benzene (35 c.c.) were condensed together in carbon disulphide (150 c.c.) by

means of aluminium chloride (35 gms.) for 6 to 12 hours, as long as hydrogen chloride was evolved. The warm mixture was decomposed with ice and a little concentrated hydrochloric acid, extracted with benzene, and the extract treated with concentrated hydrochloric acid (40 c.c.) to convert any oxide into benzophenone-*o*-dichloroarsine, dried, and concentrated. If the compound would not crystallise readily, it was again treated with hydrogen chloride (yield 25 gms.). After recrystallisation it melted at 107—108° and was only slightly yellow [Found: C = 48·1; H = 2·86; Cl = 21·6 (by titration). $C_{13}H_9OCl_2As$ requires C = 47·7; H = 2·75; Cl = 21·7 %].

*Benzophenone-o-arsinic Acid.*—A solution of benzophenone-*o*-dichloroarsine (12 gms.) in sodium hydroxide was warmed with hydrogen peroxide (20 c.c. of 20 volume), boiled with powdered charcoal for a few minutes, and acidified. The precipitated arsinic acid was recrystallised from much hot water and from dilute alcohol and dried in a vacuum at 90°; m. p. 215—219° (Found: C = 51·3; H = 3·6. Calc. for $C_{13}H_{11}O_4As$, C = 51·0; H = 3·6 %).

*Benzophenone-o-arsenious Oxide* (V).—The flocculent oxide precipitated on acidifying a filtered solution of benzophenone-*o*-dichloroarsine in aqueous sodium hydroxide began to melt at 105°, but was not completely melted at 200°. It was readily soluble in most organic solvents, from which it would not crystallise, but was insoluble in petrol and ether. The amorphous oxide was precipitated from benzene solution with petrol.

The same compound could also be obtained by reduction of hot aqueous benzophenone-*o*-arsinic acid by sulphur dioxide.

*Benzophenone-o-methylchloroarsine* (VIII).—Crude benzophenone-*o*-dichloroarsine (25 gms. in sodium hydroxide, 14 gms., and water, 50 c.c.) was shaken with methyl iodide and subsequently acidified and reduced by sulphur dioxide. The viscous substance extracted by chloroform, after crystallisation from alcohol, melted at 110—114°, and consisted chiefly of the iodoarsine. The corresponding oxide, obtained by the action of alcoholic potash, was dissolved in benzene, hydrogen chloride passed, the solvent removed, and the residue recrystallised from hot alcohol. *Benzophenone-o-methylchloroarsine* thus obtained melted at 88° (Found: Cl = 11·3. Calc., Cl = 11·6 %). Attempts at eliminating hydrogen chloride from this compound by the action of aluminium chloride on solutions in benzene, carbon disulphide, or nitrobenzene were unsuccessful. The chloroarsine decomposed on distillation.

*Benzophenone-o-methylarsinic Acid.*—The preceding oxide was boiled with hydrogen peroxide and sodium hydroxide, and the solution filtered and acidified. The tarry precipitate crystallised

slowly from water in fine, white needles, m. p. 186° (Found : C = 55·4 ; H = 4·2. $C_{14}H_{13}O_3As$ requires C = 55·3 ; H = 4·2 %).

It was not found possible to remove the elements of water from the compound with production of a ring compound.

o-*Carboxydiphenylarsinic Acid.*—The free acid was best prepared from sodium benzarsinite and diazotised aniline, the coupling being carried out by slow addition of the two solutions to ice-water, kept strictly alkaline. From the pink tar obtained on acidification, boiling water extracted carboxydiphenylarsinic acid. The extract was evaporated and the solid residue, after washing with hot water to remove sodium chloride, was recrystallised from much hot alcohol. Dried at 100°, it was a white, crystalline solid which did not melt below 300°. Analysis showed the substance to be the *anhydride* (XIII) of *o*-carboxydiphenylarsinic acid (Found : C = 54·3 ; H = 3·28. $C_{13}H_9O_3As$ requires C = 54·2 ; H = 3·12 %).

The acid was unchanged after treatment with concentrated sulphuric acid at 100°, the resulting product containing 54·0 % C and 3·18 % H, and yielding the same oxide on reduction by sulphur dioxide.

o-*Carboxydiphenylarsinous anhydride* (XII), produced by reducing the above acid in hot aqueous solution with sulphur dioxide, is a white, crystalline compound, m. p. 133°, slightly soluble in hot water, from which it crystallises well, readily soluble in alcohol, moderately soluble in hot benzene (Found : C = 57·0 ; H = 3·5. $C_{13}H_9O_2As$ requires C = 57·4 ; H = 3·3 %).

The constitution of this compound as being of the internal anhydride type rather than the isomeric hydroxide (VI), was proved by its production when *o*-carboxydiphenylchloroarsine was distilled in a vacuum. The crystalline distillate melted at 132—133°, and gave the same melting point when mixed with a specimen prepared by reduction. The anhydride was converted into the chloride by treatment with hydrogen chloride in benzene.

o-*Carboxydiphenylchloroarsine.*—The corresponding acid was prepared by the condensation of an alkaline solution of phenyldichloroarsine with a neutralised solution of diazotised anthranilic acid. After filtration, the solution was acidified, the heavy tar which separated was extracted several times with hot hydrochloric acid, and the extracts were reduced at 80° by sulphur dioxide. The reduction product was treated with hydrogen chloride in benzene solution, and the pure chloride thus obtained was a white, crystalline compound, m. p. 163°, readily soluble in alcohol, moderately soluble in hot benzene, not readily soluble in cold (Found : C = 50·1 ; H = 3·25 ; Cl = 11·4. $C_{13}H_{10}O_2ClAs$ requires C = 50·6 ; H = 3·25 ; Cl = 11·5 %).

On recrystallising a small portion from hot benzene, a product was obtained, m. p. 125° (Found : Cl = 11·3. Calc., 11·5 %).

*The acid chloride* (IV) obtained from phosphorus pentachloride and the acid suspended in chloroform, was distilled at a low pressure without much decomposition; the distillate slowly formed a paste of crystals (Found : Cl = 21·7, 22·4. Calc., 21·7 %). The isomeric benzophenone-*o*-dichloroarsine will not distil without decomposition.

*Action of Aluminium Chloride.*—A solution of the crude acid chloride in carbon disulphide was treated with anhydrous aluminium chloride in three portions with shaking. The product was warmed for 6 hours and was treated with ice-water and hydrochloric acid. The viscous residue from the benzene extract was dissolved in ethyl acetate. The crystals obtained on standing were washed with a little ether and dried, after which they melted at 98—102°, and on mixing with benzophenone-*o*-dichloroarsine at 98—104° (Found : Cl = 21·0. Calc., 21·7 %).

On evaporating the mother-liquors and treating the residue with alcoholic potash, an oxide was obtained which was identical with benzophenone-*o*-arsenious oxide. Like the oxide obtained by other methods, it was impure after precipitation from benzene solution by addition of petrol (Found : C = 57·8; H = 3·76. Calc. for $C_{13}H_9O_2As$, C = 57·4; H = 3·3 %).

In order to ascertain whether the treatment with hydrochloric acid subsequent to the condensation had reopened the ring, the experiment was repeated without the use of acid. The product was treated with alkaline hydrogen peroxide to convert it to an arsinic acid which could be more readily characterised. An almost quantitative yield of benzophenone-*o*-arsinic acid was produced melting at 205—215°, and, after mixing with the pure acid and recrystallising from methyl alcohol, at 217—218°.

It appears therefore that the condensation product did not contain any of the closed ring compound, or else that the latter is unstable to both acids and alkalis.

o-*Carboxyphenylmethylarsinous Anhydride* (XIV).—A solution of benzarsenious oxide in 20 % sodium hydroxide solution was shaken for 40 hours with the calculated quantity of methyl iodide, filtered, and acidified with hydrochloric acid and sulphur dioxide. The thick, yellow oil which separated, consisting largely of methylbenzarsenious iodide mixed with the corresponding chloride and anhydride, was dissolved in alkali and reprecipitated by sulphur dioxide. The product was purified either by distillation in a vacuum, when a vitreous distillate was obtained at 220°/15 mm., or by recrystallisation either from hot water or dilute spirit. The

vitreous product obtained by distillation crystallised slowly after treatment with benzene.

The compound is readily soluble in alcohol or hot benzene, slightly in hot water, from which it crystallises only slowly. M. p. 106°. It is converted into the chloride by treatment with hydrogen chloride in benzene solution (Found : C = 45·8; H = 3·28. $C_8H_7O_2As$ requires C = 45·7; H = 3·33 %).

o-*Carboxyphenylmethylarsinic acid* was obtained by oxidising the crude anhydride (above) by hydrogen peroxide. On cooling the solution after filtration, the acid crystallised out, and after crystallising from a little hot water a pure product, m. p. 310°, was obtained (Found : C = 39·3; H = 3·64. $C_8H_9O_4As$ requires C = 39·3; H = 3·68 %).

o-*Carboxyphenylmethylchloroarsine* was obtained by reducing the preceding acid in hydrochloric acid solution in presence of a trace of hydriodic acid, and recrystallising the product from benzene after passing hydrogen chloride. It is readily soluble in most organic solvents and in alkalis, melts at 141°, and loses hydrogen chloride on distillation in a vacuum (Found : C = 38·8; H = 3·14; Cl = 14·5; equiv. = 123. $C_8H_8O_2ClAs$ requires C = 38·9; H = 3·25; Cl = 14·4 %; equiv. = 123).

oo′-*Dicarboxydiphenylarsinic anhydride* (XVI), prepared by the condensation of diazotised anthranilic acid with an alkaline solution of benzarsenious oxide in the usual way, was recrystallised from methyl alcohol and finally from hot water. It could also be decolorised by boiling in alkaline solution with powdered charcoal, and reprecipitating the anhydride; it then melted at 255° (Found : C = 50·13, 50·34; H = 2·86, 2·75. $C_{14}H_9O_5As$ requires C = 50·57; H = 2·7 %).

The equivalent weight, determined by titration in alcohol, is low (312, 318, 305; calc. for anhydride, 332) owing to slight hydrolysis of the anhydride ring after the monosodium salt has been formed. On treating the compound with excess of alkali and back titrating with standard acid, an indefinite end-point is again observed and higher values are obtained for the equivalent than that calculated for a dibasic acid (Found, 177; calc., 166). This is because the acid liberated when the end-point is reached slowly assumes the betaine structure, and the solution again becomes alkaline.

oo′-*Dicarboxydiphenylarsinous anhydride* (XV).—A suspension of the arsinic anhydride in chloroform and phosphorus trichloride was heated for ½ hour on the water-bath, the chloroform removed, and the residue treated with boiling water for an hour. The m. p. of the anhydride thus obtained was indefinite. The pure anhydride

was obtained by hydrolysis of dicarbomethoxydiphenylchloroarsine, or by reduction of a boiling aqueous solution of the acid. When pure, it melts at 251—255°. It is insoluble in ether, benzene, chloroform, or carbon tetrachloride, but dissolves in methyl alcohol, taking up a molecule of this solvent, to which it adheres very tenaciously (Found: for product of hydrolysis of the chloroarsine ester, C = 53·36; H = 3·0; equiv., by titration in alcohol, 325, 318, 305. $C_{14}H_9O_4As$ requires C = 53·2; H = 2·85 %; equiv., for monobasic substance, 318).

*Attempts at the Preparation of Dicarboxydiphenylchloroarsine.*—An aqueous-alcoholic solution of the preceding anhydride was unaffected by hydrogen chloride. By passing hydrogen chloride into the chloroform solution obtained by reducing the arsinic anhydride by phosphorus trichloride as above, a crystalline compound was obtained, m. p. 120—140° (Found: Cl = 15·9, 12·4. Calc. for the chloroarsine, Cl = 11·0 %). On recrystallising it from hot benzene, hydrogen chloride was evolved and the residue became insoluble in benzene and chloroform and contained 1·12 or 1·9 % of chlorine, even after treating the solution with hydrogen chloride. Also on standing in air, or more slowly in a desiccator, the percentage of chlorine decreased to 6·4 and 3·0 in two specimens. On treating with water or aqueous alcohol, the compound was converted into the anhydride (XV).

oo′-*Dicarbomethoxydiphenylchloroarsine* (XVII), m.p. 184°, crystals almost insoluble in methyl alcohol, separated on passing dry hydrogen chloride into dicarboxydiphenylarsinous anhydride in this solvent, and was washed with a little alcohol and recrystallised from benzene (Found: C = 50·66; H = 3·77; Cl = 9·9; OMe = 15·7. $C_{16}H_{14}O_4ClAs$ requires C = 50·5; H = 3·7; Cl = 9·3; OMe = 16·3 %). The pure anhydride, obtained by hydrolysing the ester by alcoholic potash, was also the only product (m. p. 251—254°) of hydrolysis by the Perkin-Ziesel method. This fact illustrates the extreme readiness with which the internal anhydride ring is formed.

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# CCLXVI.—*The Viscosity and Surface Tension of Solutions of Iodine and Potassium Iodide.*

By Ernest Augustus Dancaster.

The present investigation was carried out in order to ascertain whether the viscosity and surface tension of solutions of iodine and iodides could be employed to throw light on the question of the existence of periodides in solution.

*Preparation of Materials.*—Pure iodine was resublimed with potassium iodide and dried over concentrated sulphuric acid.

Potassium iodide containing only traces of sodium iodide was dried over sulphuric acid.

Absolute alcohol was used without any further purification.

Pure methyl alcohol was dried over quicklime and fractionally distilled. The fraction, b. p. 65—65·5°, was free from acetone and ethyl alcohol.

Ordinary distilled water was fractionally distilled and the middle fraction collected.

*Experimental Method.*—Two sets of solutions were examined. (1) Aqueous ethyl-alcoholic solutions of iodine and potassium iodide, in each of which the alcohol was 70 per cent. by volume and the sum of the iodine and iodide 0·1 gram-equivalent per litre. The density and viscosity of these solutions were determined at 25·6°. (2) Pure methyl-alcoholic solutions of iodine and potassium iodide, in each of which the sum of the iodine and iodide was 1·0 gram-equivalent per litre. The density, viscosity, and surface tension of these solutions were determined at 25·6°. Two viscosimeters of the Ostwald type were employed, and the surface tension was determined by means of Sugden's modification of Jaeger's method (J., 1922, **121**, 858). The results are recorded in Tables I and II. The concentrations of iodine (*a*) and potassium iodide (*b*) are expressed in gms. per litre.

Table I.

Aqueous alcoholic solutions containing 70% (by volume) of ethyl alcohol.

| *a*. | *b*. | $d^{25·6°}$. | $\eta^{25·6°} \times 10^3$. | *a*. | *b*. | $d^{25·6°}$. | $\eta^{25·6°} \times 10^3$. |
|---|---|---|---|---|---|---|---|
| 12·692 | 0·000 | 0·8912 | 21·51 | 9·067 | 4·743 | 0·8925 | 21·58 |
| 10·582 | 2·767 | 0·8919 | 21·54 | 8·464 | 5·534 | 0·8926 | 21·58 |
| 10·390 | 3·018 | 0·8921 | 21·57 | 7·616 | 6·641 | 0·8927 | 21·55 |
| 10·154 | 3·320 | 0·8922 | 21·59 | 6·347 | 8·302 | 0·8931 | 21·51 |
| 9·875 | 3·685 | 0·8923 | 21·54 | 2·538 | 13·282 | 0·8936 | 21·47 |
| 9·520 | 4·151 | 0·8924 | 21·56 | 0·000 | 16·602 | 0·8938 | 21·33 |

TABLE II.

Solutions in pure methyl alcohol.

| $a$. | $b$. | $d^{25\cdot6°}$. | $\eta^{25\cdot6°} \times 10^4$. | $\gamma^{25\cdot6°}$. | $a$. | $b$. | $d^{25\cdot6°}$. | $\eta^{25\cdot6°} \times 10^4$. | $\gamma^{25\cdot6°}$. |
|---|---|---|---|---|---|---|---|---|---|
| 126·92 | 0·00 | 0·8899 | 60·56 | 23·44 | 98·76 | 36·86 | 0·8993 | 65·68 | — |
| 112·86 | 18·44 | 0·8950 | 62·86 | 23·29 | 95·19 | 41·50 | 0·9003 | 65·79 | 23·39 |
| 111·07 | 20·75 | 0·8958 | 63·22 | 23·39 | 90·62 | 47·49 | 0·9025 | 66·23 | 23·40 |
| 108·775 | 23·74 | 0·8975 | 63·56 | 23·33 | 84·66 | 55·30 | 0·9052 | 66·96 | 23·44 |
| 105·73 | 27·73 | 0·8976 | 64·25 | 23·37 | 76·16 | 66·42 | 0·9070 | 68·20 | 23·37 |
| 101·54 | 33·20 | 0·8978 | 65·14 | 23·32 | 63·46 | 83·01 | 0·9102 | 69·72 | 23·47 |

The density, viscosity, and surface tension of pure methyl alcohol were also determined. This was done not only for the purpose of testing the methods employed, but also to serve as a further proof of the purity of the methyl alcohol. The values found were: $d^{25\cdot6°}$ 0·7874, $\eta^{25\cdot6°}$ 0·005613, $\gamma^{25\cdot6°}$ 22·58.

*Discussion of Results.*

It is evident that neither the viscosity nor the surface tension of solutions of iodine and iodides can be employed to detect the formation of periodides in solution. The compound $KI_3$ was undoubtedly formed in the solutions investigated; and yet in the case of the *N*-methyl-alcoholic solutions, except for a slight hump in the viscosity–concentration curve at about 0·22 mol. of potassium iodide and 0·78 mol. of iodine per litre, there is little evidence of any such combination, and the curve shows very little deviation from the straight line. The results obtained with the *N*/10-solutions are even less conclusive, because the small deviations found are not greater than those obtained through unavoidable experimental error.

The surface tensions, also, show very little variation. They have practically the same value in the case of the mixtures of iodine and potassium iodide as in that of pure iodine.

A pure *N*-solution of potassium iodide could not be obtained in the solvent used, and therefore the surface tension of such a solution cannot be ascertained for comparison with those of the mixtures.

The values of the density, viscosity, and surface tension obtained during this investigation agree fairly closely with the means of those recorded by other workers, which vary considerably.

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# CCLXVII.—*Chloro-Perbromide Equilibria.*

By Ernest Augustus Dancaster.

A considerable amount of work has been done on the thermal dissociation of perbromides and periodides in solution by Roloff (*Z. physikal. Chem.*, 1894, **13**, 341), Jakowkin (*ibid.*, 1894, **13**, 539; 1895, **18**, 585; 1896, **20**, 19), Herz and Bulla (*Z. anorg. Chem.*, 1911, **71**, 254), Bray and MacKay (*J. Amer. Chem. Soc.*, 1910, **32**, 1207), van Name and Brown (*Amer. J. Sci.*, 1917, [iv], **44**, 105) and others. Very little, however, has been done on the perhalogen compounds containing two different halogens. Berthelot (*Compt. rend.*, 1882, **94**, 1619; 1885, **100**, 761) has shown that a concentrated solution of barium chloride or strontium chloride absorbs a considerable amount of bromine, apparently with the formation of perbromides, and Jakowkin has determined the dissociation of the compounds $NaClI_2$, $KBrI_2$, and $KClBr_2$ at 25°.

The objects of the present investigation were to ascertain whether (1) chloro-perbromides present any abnormalities, (2) the chloro-perbromides of cadmium and mercury show corresponding abnormalities to those of the perbromides and periodides of those metals, and (3) other abnormal chloro-perbromides exist. The perhalogen compounds of magnesium and aluminium have not been previously investigated.

*Preparation of the Materials.*—The carbon tetrachloride was repeatedly shaken with alcoholic potash, thoroughly washed, dried over phosphorus pentoxide, and fractionated. The product had no action on bromine.

The bromine (A.R. quality) was agitated with potassium bromide and fractionated. The middle fraction was dried over phosphorus pentoxide and again fractionated. The middle fraction now had a constant melting point at −7·2°.

The iodine was mixed with potassium iodide and sublimed, and the material thus purified was dried over concentrated sulphuric acid.

The chlorides employed were the purest obtainable. The aluminium chloride was redistilled and the remaining salts were all submitted to two or more recrystallisations before use.

*Experimental Method.*—The method employed was that of Jakowkin. The titrable halogen in the aqueous layer and the free bromine in the carbon tetrachloride layer were determined and the dissociation constant, $K_1$, was then calculated from the formula

$$K_1 = (na - b + x)x/(b - x),$$

where $n$ is the valency of the metal under consideration, $a$ is the molar concentration of the chloride, and $b$ and $x$ are those of the titrable bromine and of the free bromine in the aqueous layer.

The solutions were made by dissolving a weighed amount of the salt in water and diluting to the required volume. The aluminium chloride solution was filtered after several days to remove aluminium hydroxide. The aluminium and chlorine were then determined and the amount of hydrogen chloride present was calculated. The exact concentrations of the cadmium, mercury, magnesium, and calcium solutions were also determined by gravimetric analysis.

A mixture of 50 c.c. of the chloride solution under investigation and 25 c.c. of a concentrated solution of bromine in carbon tetrachloride was shaken for 5 minutes and left in the thermostat at 25° for about an hour. The bromine in 10 c.c. of each layer was then estimated with potassium iodide solution and sodium thiosulphate. (In the case of copper chloride, the sample from the aqueous layer was boiled and the evolved bromine passed into the potassium iodide solution). After each determination, 10 c.c. of the original chloride solution and 10 c.c. of pure dry carbon tetrachloride were added to the remaining mixture and the whole process was repeated. This was continued until the series was completed.

The following table shows the mean values of $K_1$ obtained with different concentrations of the halides employed.

| | Dissociation constant, $K_1$, at 25°. | | | | |
|---|---|---|---|---|---|
| Halide. | 0·025*M*. | 0·05*M*. | 0·1*M*. | 0·5*M*. | 1·0*M*. |
| $CuCl_2$ | — | — | 0·712 | — | 0·7125 |
| $MgCl_2$ | — | 0·719 | 0·725 | 0·725 | 0·716 |
| $CaCl_2$ | — | — | 0·723 | 0·724 | 0·731 |
| $SrCl_2$ | 0·734 | — | 0·711 | 0·719 | 0·724 |
| $BaCl_2$ | 0·718 | — | 0·730 | 0·729 | 0·729 |
| $CdCl_2$ | — | — | 1·101 | — | 1·600 |
| $HgCl_2$ | — | — | 0·938 | — | 1·044 |
| $AlCl_3$ | — | — | 0·723 | — | — |

The full results obtained are given in the table below, where $b$ is the molar concentration of titrable bromine in the aqueous layer, $g$ is the molar concentration of free bromine in the carbon tetrachloride layer, and $c$ is the distribution coefficient, derived from Jakowkin's results.

$x$, the molar concentration of the free bromine in the aqueous layer, is equal to $g/c$.

The values of $K_1$ enclosed in brackets are not included in the mean values.

## Dissociation of $CuCl_2Br_4$ at 25°.

| $a$ = 1·0003$M$-$CuCl_2$. | | | | $a$ = 0·0998$M$-$CuCl_2$. | | | |
|---|---|---|---|---|---|---|---|
| $b$. | $g$. | $c$. | $K_1$. | $b$. | $g$. | $c$. | $K_1$. |
| 0·05622 | 0·7131 | 46·9 | 0·725 | 0·03460 | 0·8236 | 30·1 | 0·727 |
| 0·03763 | 0·4519 | 45·6 | 0·705 | 0·02153 | 0·4903 | 29·0 | 0·712 |
| 0·02390 | 0·2793 | 44·75 | 0·701 | 0·01343 | 0·2921 | 28·3 | (0·652) |
| 0·015055 | 0·1752 | 44·2 | 0·711 | 0·008450 | 0·1849 | 28·0 | 0·708 |
| 0·009525 | 0·1105 | 43·8 | 0·718 | 0·005270 | 0·1143 | 27·8 | 0·705 |
| 0·006080 | 0·06973 | 43·5 | 0·715 | 0·003290 | 0·07130 | 27·6 | 0·726 |
| | | Mean | 0·7125 | | | Mean | 0·712 |

## Dissociation of $MgCl_2Br_4$ at 25°.

| $a$ = 1·0456$M$-$MgCl_2$. | | | | $a$ = 0·4902$M$-$MgCl_2$. | | | |
|---|---|---|---|---|---|---|---|
| 0·08162 | 1·018 | 48·6 | 0·701 | 0·08047 | 1·297 | 37·3 | 0·711 |
| 0·05019 | 0·6103 | 46·4 | 0·729 | 0·05198 | 0·7965 | 35·4 | 0·726 |
| 0·03163 | 0·3654 | 45·1 | 0·712 | 0·03243 | 0·4820 | 34·2 | 0·739 |
| 0·01890 | 0·2186 | 44·35 | 0·728 | 0·02054 | 0·2953 | 33·4 | 0·732 |
| 0·01174 | 0·1308 | 43·9 | 0·709 | 0·01302 | 0·1831 | 33·0 | 0·723 |
| | | Mean | 0·716 | 0·008051 | 0·1120 | 32·8 | 0·718 |
| | | | | | | Mean | 0·725 |
| $a$ = 0·1090$M$-$MgCl_2$. | | | | $a$ = 0·0523$M$-$MgCl_2$. | | | |
| 0·08287 | 2·265 | 34·9 | 0·721 | 0·05081 | 1·421 | 31·8 | 0·719 |
| 0·05331 | 1·321 | 31·8 | 0·726 | 0·03290 | 0·8658 | 30·0 | 0·718 |
| 0·03500 | 0·8176 | 30·1 | 0·728 | 0·02061 | 0·5221 | 28·9 | 0·724 |
| 0·02215 | 0·4984 | 29·0 | 0·738 | 0·01293 | 0·32025 | 28·3 | 0·722 |
| 0·013615 | 0·2978 | 28·4 | 0·720 | 0·007915 | 0·1919 | 27·8 | 0·708 |
| 0·008746 | 0·1882 | 28·0 | 0·717 | 0·004815 | 0·1160 | 27·55 | 0·725 |
| 0·005326 | 0·1141 | 27·8 | 0·728 | | | Mean | 0·719 |
| | | Mean | 0·725 | | | | |

## Dissociation of $CaCl_2Br_4$ at 25°.

| $a$ = 1·0014$M$-$CaCl_2$. | | | | $a$ = 0·5166$M$-$CaCl_2$. | | | |
|---|---|---|---|---|---|---|---|
| 0·06579 | 0·8559 | 47·7 | 0·733 | 0·05040 | 0·7180 | 33·9 | 0·726 |
| 0·04288 | 0·5394 | 46·05 | 0·741 | 0·03253 | 0·4468 | 32·9 | 0·725 |
| 0·02722 | 0·3321 | 45·0 | 0·738 | 0·02066 | 0·2788 | 32·2 | 0·737 |
| 0·01655 | 0·1942 | 44·2 | 0·720 | 0·01287 | 0·1686 | 31·8 | 0·719 |
| 0·01032 | 0·1209 | 43·9 | 0·726 | 0·008040 | 0·1035 | 31·5 | 0·711 |
| 0·006471 | 0·0746 | 43·6 | 0·730 | | | Mean | 0·724 |
| | | Mean | 0·731 | | | | |
| $a$ = 0·1242$M$-$CaCl_2$. | | | | $a$ = 0·1242$M$-$CaCl_2$. | | | |
| 0·03505 | 0·7881 | 30·0 | 0·717 | 0·008746 | 0·1822 | 28·0 | 0·715 |
| 0·02197 | 0·4769 | 28·9 | 0·733 | 0·005455 | 0·1133 | 27·8 | 0·730 |
| 0·01413 | 0·2996 | 28·4 | 0·721 | | | Mean | 0·723 |

## Dissociation of $SrCl_2Br_4$ at 25°.

| $a$ = 1·0003$M$-$SrCl_2$. | | | | $a$ = 0·4997$M$-$SrCl_2$. | | | |
|---|---|---|---|---|---|---|---|
| $b$. | $g$. | $c$. | $K_1$. | $b$. | $g$. | $c$. | $K_1$. |
| 0·05777 | 0·7166 | 46·3 | 0·717 | 0·07464 | 1·061 | 33·3 | 0·712 |
| 0·03636 | 0·4387 | 44·9 | 0·725 | 0·04807 | 0·6377 | 31·7 | 0·699 |
| 0·02280 | 0·2675 | 43·9 | 0·724 | 0·02828 | 0·3701 | 30·8 | 0·727 |
| 0·01440 | 0·1657 | 43·4 | 0·718 | 0·01716 | 0·2098 | 30·2 | (0·673) |
| 0·008775 | 0·1007 | 43·1 | 0·723 | 0·009910 | 0·1165 | 29·9 | (0·643) |
| 0·005496 | 0·06296 | 42·8 | 0·730 | 0·005310 | 0·06532 | 29·7 | 0·706 |
| 0·003425 | 0·03929 | 42·8 | 0·732 | 0·003119 | 0·03824 | 29·7 | 0·701 |
| | | Mean | 0·724 | 0·001718 | 0·02130 | 29·7 | 0·715 |
| | | | | | | Mean | 0·719 |

$a = 0{\cdot}1276M$-$SrCl_2$.

| | | | |
|---|---|---|---|
| 0·04875 | 1·126 | 31·1 | 0·705 |
| 0·030415 | 0·6645 | 29·6 | 0·697 |
| 0·01843 | 0·3920 | 28·7 | 0·717 |
| 0·01146 | 0·2379 | 28·2 | 0·704 |
| 0·006589 | 0·1359 | 27·8 | 0·729 |
| 0·004018 | 0·08121 | 27·55 | 0·721 |
| 0·002270 | 0·04577 | 27·55 | 0·694 |
| 0·001331 | 0·02709 | 27·55 | 0·720 |
| | | Mean | 0·711 |

$a = 0{\cdot}0250M$-$SrCl_2$.

| | | | |
|---|---|---|---|
| 0·08746 | 3·008 | 36·7 | 0·708 |
| 0·05871 | 1·812 | 32·9 | 0·750 |
| 0·03792 | 1·088 | 30·65 | 0·744 |
| | | Mean | 0·734 |

## Dissociation of $BaCl_2Br_4$ at 25°.

$a = 1{\cdot}00025M$-$BaCl_2$.

| | | | |
|---|---|---|---|
| 0·05641 | 0·7321 | 47·9 | 0·728 |
| 0·03593 | 0·4523 | 46·3 | 0·737 |
| 0·02279 | 0·2772 | 45·4 | 0·727 |
| 0·01402 | 0·1686 | 44·9 | 0·729 |
| 0·008660 | 0·1029 | 44·4 | 0·729 |
| 0·005405 | 0·06355 | 44·2 | 0·724 |
| | | Mean | 0·729 |

$a = 0{\cdot}5002M$-$BaCl_2$.

| | | | |
|---|---|---|---|
| 0·08737 | 1·2695 | 34·0 | 0·713 |
| 0·05505 | 0·7639 | 32·2 | 0·734 |
| 0·03107 | 0·4114 | 30·9 | 0·736 |
| 0·01975 | 0·2557 | 30·4 | 0·733 |
| 0·01244 | 0·1546 | 30·0 | 0·702 |
| 0·00809 | 0·09623 | 29·8 | (0·663) |
| | | Mean | 0·729 |

$a = 0{\cdot}1003M$-$BaCl_2$.

| | | | |
|---|---|---|---|
| 0·01590 | 0·3620 | 29·0 | 0·720 |
| 0·009850 | 0·2235 | 28·9 | 0·724 |
| 0·006099 | 0·1357 | 28·3 | 0·729 |
| 0·003700 | 0·0815 | 27·7 | (0·773) |
| 0·002350 | 0·05044 | 27·5 | 0·704 |
| | | Mean | 0·730 |

$a = 0{\cdot}0251M$-$BaCl_2$.

| | | | |
|---|---|---|---|
| 0·2190 | 0·6078 | 29·6 | 0·731 |
| 0·01380 | 0·3672 | 28·4 | 0·731 |
| 0·00840 | 0·2225 | 28·0 | 0·708 |
| 0·005150 | 0·1334 | 27·5 | (0·81) |
| 0·003170 | 0·08048 | 27·2 | (0·67) |
| 0·001910 | 0·048625 | 27·2 | 0·714 |
| 0·001160 | 0·02962 | 27·2 | 0·724 |
| 0·000705 | 0·01776 | 27·2 | 0·701 |
| | | Mean | 0·718 |

## Dissociation of $CdCl_2Br_4$ at 25°.

$a = 1{\cdot}1298M$-$CdCl_2$.

| | | | |
|---|---|---|---|
| 0·06186 | 1·299 | 50·1 | 1·612 |
| 0·04036 | 0·8081 | 47·5 | 1·594 |
| 0·02604 | 0·4972 | 45·9 | 1·598 |
| 0·01602 | 0·2989 | 44·8 | 1·605 |
| 0·01006 | 0·1845 | 44·1 | 1·600 |
| 0·006180 | 0·1125 | 43·9 | 1·589 |
| | | Mean | 1·600 |

$a = 0{\cdot}1071M$-$CdCl_2$.

| | | | |
|---|---|---|---|
| 0·03848 | 0·9905 | 30·7 | 1·079 |
| 0·02431 | 0·6008 | 29·4 | 1·107 |
| 0·01519 | 0·3594 | 28·6 | 1·015 |
| 0·009176 | 0·2155 | 28·1 | 1·080 |
| 0·0054605 | 0·1293 | 27·8 | 1·225 |
| 0·00320 | 0·07703 | 27·7 | 1·100 |
| | | Mean | 1·101 |

## Dissociation of $HgCl_2Br_4$ at 25°.

$a = 0{\cdot}17322M$-$HgCl_2$.

| | | | |
|---|---|---|---|
| 0·05262 | 1·288 | 32·4 | 1·030 |
| 0·03453 | 0·7921 | 30·6 | 1·011 |
| 0·02142 | 0·4795 | 29·6 | 1·059 |
| 0·01364 | 0·2858 | 28·9 | (0·904) |
| 0·008166 | 0·1736 | 28·5 | 1·101 |
| 0·004705 | 0·09908 | 28·2 | 1·017 |
| | | Mean | 1·044 |

$a = 0{\cdot}10054M$-$HgCl_2$.

| | | | |
|---|---|---|---|
| 0·03162 | 0·7862 | 29·8 | 0·986 |
| 0·01991 | 0·4720 | 28·9 | 0·901 |
| 0·01244 | 0·2889 | 28·3 | 0·911 |
| 0·006895 | 0·16575 | 27·9 | (1·246) |
| 0·004305 | 0·09809 | 27·7 | 0·930 |
| 0·002625 | 0·05987 | 27·55 | 0·964 |
| 0·001615 | 0·03665 | 27·55 | 0·937 |
| 0·001015 | 0·02303 | 27·55 | 0·938 |
| | | Mean | 0·938 |

## Dissociation of $AlCl_3Br_6$ at 25°.

$a = 0{\cdot}1048M$-$AlCl_3 + 0{\cdot}0247M$-HCl.

| | | | |
|---|---|---|---|
| 0·03899 | 0·8101 | 30·0 | 0·736 |
| 0·02452 | 0·4914 | 29·0 | 0·739 |
| 0·01544 | 0·2961 | 28·3 | 0·702 |
| 0·009753 | 0·1866 | 27·9 | 0·724 |
| 0·006098 | 0·1149 | 27·7 | 0·717 |
| 0·003859 | 0·072485 | 27·6 | 0·720 |
| | | Mean | 0·723 |

*Discussion of Results.*

It is evident from the results that the chlorides of copper, calcium, strontium, barium, magnesium, and aluminium all behave "normally," *i.e.*, they give at 25° a value of $K_1$ which agrees approximately with that obtained by Jakowkin for the compound $KClBr_2$ (about 0·73). The chlorides of cadmium and mercury, however, behave abnormally; as found by van Name and Brown for the perbromides and periodides of these metals, the value of $K_1$ is in each case much greater than that given by the salts which behave "normally," and this value increases with the concentration of the chlorides. Owing to the greater solubility of mercuric chloride, the value of $K_1$ was obtained for a much greater concentration than could be obtained with mercuric bromide. There are still several halides to be investigated before those of cadmium and mercury can be said to be the only ones that are "abnormal." Most of the halides that have not been examined present special difficulties because of hydrolysis, or some other reaction, taking place in aqueous solution. It is proposed to extend the investigation to these salts by making use of non-aqueous solutions.

As van Name and Brown have shown, if we accept their view that the salts of cadmium and mercury show their abnormality towards the trihalide equilibrium because "the power to unite with the halogen is possessed only by the normal molecules and ions," we can calculate the "active fraction," *i.e.*, that portion of the total halide concentration which is in the form of simple molecules.

This value has been calculated for the chlorobromides of cadmium and mercury and the results are given below.

| $CdCl_2$. | $Br_2$. | Active fraction %. | $HgCl_2$. | $Br_2$. | Active fraction %. |
|---|---|---|---|---|---|
| 1·1298 | 0·0259 | 46·2 | 0·17322 | 0·0397 | 70·5 |
| | 0·00256 | 45·4 | | 0·00357 | 69·5 |
| | 0·0 | 45·0 | | 0·0 | 69·3 |
| 0·1071 | 0·0323 | 66·8 | 0·10054 | 0·0264 | 77·9 |
| | 0·00278 | 65·9 | | 0·00084 | 77·3 |
| | 0·0 | 65·8 | | 0·0 | 77·3 |

The values for pure solutions of cadmium and mercury chlorides, *i.e.*, for solutions containing no free bromine, were obtained by extrapolation. The "active fraction" in a pure solution of either chloride increases with the dilution, as it does in the case of the bromides and iodides of these metals, but it is considerably larger in the case of the chlorides than in that of the bromides, and the latter have been shown by van Name and Brown to have a much larger "active fraction" than the iodides.

*Summary.*

The chlorine–bromide equilibrium at 25° of a number of chlorides has been studied, and the value of $K_1$ determined. Except for Jakowkin's work on $NaClBr_2$, the chloro-perbromides had not been previously investigated, and the magnesium and aluminium halides had not been investigated in any case.

The chlorides of copper, magnesium, calcium, strontium, barium, and aluminium behave normally, *i.e.*, the value of $K_1$ in solutions up to a concentration of 1 gram-molecule per litre is the same as that found for the chlorides of the alkali metals. In the case of the chlorides of cadmium and mercury the value of $K_1$ is much higher, and increases considerably with increase of concentration.

The percentage of complex molecules and ions in solutions of the chlorides of cadmium and mercury has been determined by van Name and Brown's method. It has been found that the percentage of simple molecules and ions in a pure solution of cadmium or mercury chloride increases with the dilution.

The author wishes to express his thanks to Dr. G. Senter and Dr. S. Sugden for their valuable advice and guidance throughout the work

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## CCLXVIII.—*The Dependence on Pressure of the Adiabatic Cooling of some Organic Substances.*

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THE method adopted in the investigation of the adiabatic compression and expansion of water (J., 1923, **123**, 2717) has been employed in the investigation of changes of temperature of some other substances: phenol, benzene, urethane, *p*-toluidine, and mixtures of benzene with urethane and of phenol with *p*-toluidine, further of ethyl alcohol, glycerol, and castor oil. The experiments with the first four substances and with their mixtures were carried out at 80—90°, temperatures at which the substances remained liquid even at the highest pressures employed; therefore all the results obtained relate to the liquid state. The adiabatic cooling of ethyl alcohol was investigated at 30°, of glycerol at 25° and 98·2°, and of castor oil at 0°. Pure ethyl alcohol crystallises at — 112° (Pushin and Glagoleva, *J. Russ. Chem. Soc.*, 1915, **47**, 100) and pure glycerol at 18° (*idem*, J., 1922, **121**, 2813). The dependence

of the temperature of crystallisation of alcohol and glycerol on pressure has not yet been investigated. For most organic substances, however, the temperature of crystallisation rises less than 75° with increasing pressure up to 3000 kg./cm.$^2$. Therefore it is most probable that both ethyl alcohol at 30° and glycerol at 98·2° were in the liquid state during our investigations. At 25° and pressures higher than 1000 kg./cm.$^2$, glycerol was undoubtedly in the supercooled state, and so also must have been the castor oil at 0° and high pressures.

The change of temperature during the adiabatic process was measured by means of a thermo-element and registered photographically. Photographs showed clearly that the galvanometer, after the deflection due to the adiabatic process, remained motionless for a considerable time (about 30 seconds) and therefore that the thermo-element, centrally situated in the substance under investigation, only slowly acquired the temperature of the surroundings (the glass vessel, the bomb, and the liquid, usually castor oil, employed for the transmission of pressure). Therefore the maximal change of temperature due to the adiabatic process could be determined with great precision.

Tables I and II and Figs. 1 and 2 show the results of the investigation. In the tables, $p$ is the mean value of the pressures at the beginning and the end of the adiabatic process, $\Delta p$ the difference between these two pressures,* $\Delta t$ the measured change of temperature of the substance during the process, $(dt/dp)_s$ the change of the temperature of the substance corresponding to a change of pressure of 1 kg./cm.$^2$ at a pressure $p$. It should be noticed that the values $(dt/dp)_s$ shown in the tables do not refer to the temperatures $t = 25°$, 30°, 80°, and 90°, but to the mean temperature, $t - \Delta t/2$, which differs by 1—3° from that in the tables.

TABLE I.

Change of temperature by adiabatic expansion (and also by adiabatic compression in the case of ethyl alcohol).

| $\Delta p$ (kg./cm.$^2$). | $\Delta t°$. | $p$ (kg./cm.$^2$). | $(dt/dp)_s$ $\times 10^5$. | $\Delta p$ (kg./cm.$^2$). | $\Delta t°$. | $p$ (kg./cm.$^2$). | $(dt/dp)_s$ $\times 10^5$. |
|---|---|---|---|---|---|---|---|
| Phenol at 80°. | | | | | | | |
| 380 | 3·792° | 510 | 997° | 472 | 3·004° | 2186 | 636° |
| 415 | 3·773 | 878 | 909 | 617 | 4·064 | 2293 | 659 |
| 475 | 3·978 | 1293 | 837 | 405 | 2·602 | 2403 | 642 |
| 507 | 3·844 | 1753 | 758 | 510 | 3·317 | 2467 | 650 |
| 255 | 1·738 | 2078 | 681 | 457 | 2·924 | 2627 | 640 |
| 360 | 2·437 | 2120 | 677 | 325 | 1·965 | 2868 | 605 |

* The initial and final pressures, $p_1$ and $p_2$, recorded by the gauge before and after the adiabatic process are given by the equations $p_1 = p + \Delta p/2$; $p_2 = p - \Delta p/2$.

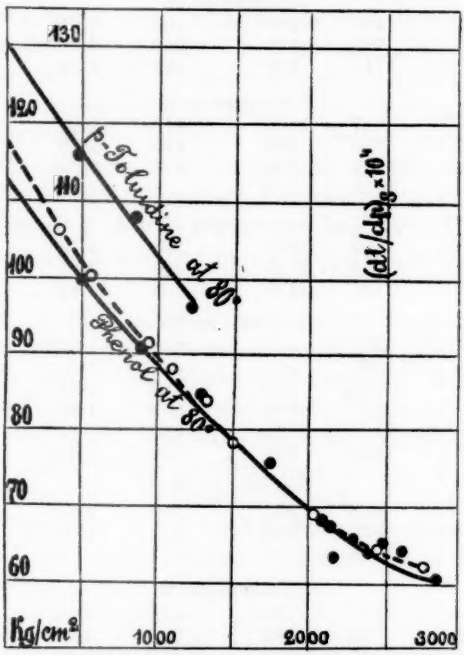
| $\Delta p$ (kg./cm.²). | $\Delta t°$. | $p$ (kg./cm.²). | $(dt/dp)_s$ $\times 10^5$. | $\Delta p$ (kg./cm.²). | $\Delta t°$. | $p$ (kg./cm.²). | $(dt/dp)_s$ $\times 10^5$. |
|---|---|---|---|---|---|---|---|
| | | | *p*-Toluidine at 80°. | | | | |
| 413 | 4·80° | 486 | 1161° | 398 | 3·82° | 1234 | 961° |
| 375 | 4·04 | 862 | 1077 | | | | |
| | | | Mixture of 75 mol. % of phenol and 25 mol. % of *p*-toluidine at 80°. | | | | |
| 345 | 3·66° | 363 | 1060° | 392 | 3·06° | 1506 | 780° |
| 378 | 3·78 | 549 | 1000 | 475 | 3·26 | 2037 | 687 |
| 410 | 3·75 | 960 | 915 | 393 | 2·54 | 2452 | 647 |
| 456 | 4·01 | 1110 | 879 | 370 | 2·30 | 2800 | 623 |
| 350 | 2·91 | 1320 | 832 | | | | |
| | | | Benzene at 90°. | | | | |
| 330 | 6·67° | 470 | 202° | 460 | 5·62° | 1960 | 122° |
| 380 | 6·70 | 785 | 176 | 547 | 5·62 | 2738 | 103 |
| 410 | 6·23 | 1145 | 152 | 465 | 4·38 | 3233 | 94 |
| | | | Urethane at 80°. | | | | |
| 355 | 3·89° | 447 | 1096° | 443 | 3·20° | 1928 | 721° |
| 447 | 4·40 | 688 | 985 | 480 | 3·12 | 2187 | 651 |
| 465 | 3·95 | 1107 | 850 | 430 | 2·73 | 2620 | 634 |
| 495 | 3·79 | 1488 | 767 | | | | |
| | | | Mixture of 75 mol. % of benzene and 25 mol. % of urethane at 90°. | | | | |
| 355 | 7·00° | 382 | 1970° | 398 | 4·54° | 1850 | 1140° |
| 424 | 6·07 | 750 | 1720 | 422 | 4·07 | 2650 | 960 |
| 371 | 5·48 | 1127 | 1480 | 403 | 3·42 | 3142 | 850 |
| | | | Glycerol at 25°. | | | | |
| 460 | 1·91° | 375 | 416° | 342 | 1·19° | 1529 | 348° |
| 357 | 1·45 | 529 | 405 | 465 | 1·55 | 1907 | 334 |
| 372 | 1·49 | 776 | 399 | 482 | 1·56 | 2009 | 325 |
| 385 | 1·49 | 877 | 387 | 502 | 1·54 | 2351 | 307 |
| 398 | 1·49 | 1141 | 375 | 542 | 1·65 | 2476 | 304 |
| 450 | 1·66 | 1265 | 368 | 584 | 1·73 | 3000 | 296 |
| | | | Glycerol at 98·2°. | | | | |
| 435 | 2·49° | 458 | 573° | 400 | 1·89° | 1500 | 473° |
| 330 | 1·76 | 825 | 533 | 435 | 1·95 | 1893 | 448 |
| 365 | 1·85 | 1148 | 506 | | | | |
| | | | Castor oil at 0°. | | | | |
| 355 | 2·55° | 362 | 720° | 483 | 2·45° | 2029 | 506° |
| 518 | 3·44 | 729 | 664 | 315 | 1·49 | 2412 | 472 |
| 417 | 2·53 | 1157 | 608 | 440 | 2·00 | 2730 | 455 |
| 488 | 2·63 | 1579 | 538 | 205 | 0·94 | 3042 | 458 |
| | | | Ethyl alcohol at 30°. | | | | |
| By adiabatic expansion. | | | | By adiabatic compression. | | | |
| 285 | 3·72° | 262 | 1304° | 380 | 4·68° | 365 | 1233° |
| 481 | 5·36 | 592 | 1114 | 390 | 4·10 | 725 | 1052 |
| 392 | 4·24 | 736 | 1081 | 409 | 4·16 | 775 | 1017 |
| 545 | 5·21 | 1052 | 956 | 485 | 4·31 | 1125 | 887 |
| 372 | 2·94 | 1454 | 791 | 580 | 4·47 | 1560 | 770 |
| 845 | 6·22 | 1913 | 736 | 705 | 4·94 | 2042 | 700 |
| 865 | 6·12 | 2107 | 708 | | | | |
| 473 | 3·17 | 2228 | 670 | | | | |
| 560 | 3·62 | 2693 | 645 | | | | |

From Table I and Fig. 1 it can be seen that with increasing pressure the function $(dt/dp)_s$ for phenol decreases, as is the case with all the

liquids investigated (except water at temperatures below 37°). The value of the function is 0·00999 at a pressure of 500 kg./cm.$^2$ and diminishes to 0·00677 at a pressure of 2120 kg./cm.$^2$, which is only two-thirds of the former value.

The curve for phenol in the direction of adiabatic cooling shows a peculiarity which is probably due to the existence of another modification of phenol at higher pressures. And indeed, as determinations of its melting point at high pressures have shown,* phenol

FIG. 1.



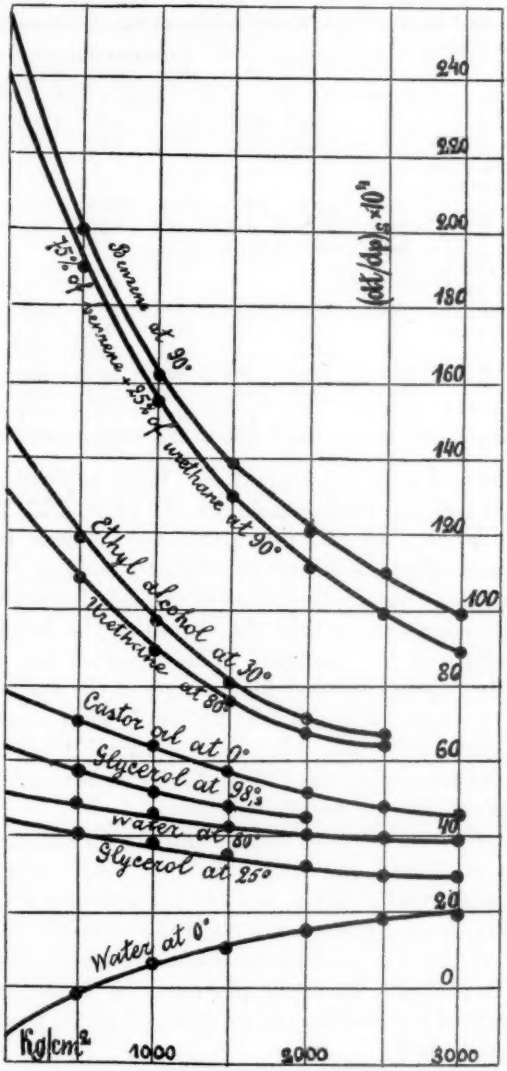

*Coefficient of adiabatic cooling as a function of pressure.*
*-o---o-- mixture: 75 mol. % of phenol+25 mol. % of p-toluidine.*

changes under a pressure of 2250 kg./cm.$^2$ and at a temperature of 64·4° to a denser modification, phenol II. Under pressures higher than 2250 kg./cm.$^2$ the above-named modification is stable. At the same pressure, the curve of the coefficient of adiabatic cooling becomes almost horizontal, that is, the relative rate of cooling of phenol (for a change of pressure of 1 kg./cm.$^2$) becomes almost independent of pressure.

* The results will be published separately. See also Tammann, "Kristallisieren und Schmelzen," 1903, 308; *Z. physikal. Chem.*, 1910, **75**, 75; Bridgman, *Proc. Amer. Acad.*, 1915, **51**, 112.

It can be seen from the tables and figures given above that benzene has the greatest coefficient of adiabatic cooling of all the substances

FIG. 2.




*Coefficient of adiabatic cooling as a function of pressure.*

which have been investigated. The value of $(dt/dp)_s$ for benzene is 0·0200 at a pressure of 500 kg./cm.$^2$ and a temperature of 90°. Urethane, phenol, and *p*-toluidine have a coefficient almost two

## TABLE II.

Change of temperature by adiabatic expansion of substances.

The values of $(dt/dp)_s$ at $p = 1$ kg./cm.$^2$ are obtained by a graphic extrapolation, and therefore are less accurate than all the other values, which are obtained by a graphic interpolation of the experimental data.

| Substance. | Temp. | Pressure (kg./cm.$^2$). 1 | 500 | 1000 | 1500 | 2000 | 2500 | 3000 |
|---|---|---|---|---|---|---|---|---|
| | | $dt/dp \times 10^5$. | | | | | | |
| Benzene | 90° | 2550° | 2000° | 1620° | 1390° | 1210° | 1090° | 990° |
| Urethane | 80 | 1300 | 1072 | 884 | 765 | 702 | 639 | |
| Mixture, 75 mol. % of benzene + 25 mol. % of urethane | 90 | 2400 | 1890 | 1560 | 1300 | 1110 | 990 | 880 |
| Phenol | 80 | 1130 | 999 | 883 | 802 | 726 | 648 | |
| *p*-Toluidine | 80 | 1300 | 1158 | 1034 | | | | |
| Mixture, 75 mol. % of phenol + 25 mol. % of *p*-toluidine | 80 | 1160 | 1016 | 905 | 782 | 691 | 644 | |
| Ethyl alcohol | 30 | 1450 | 1180 | 965 | 805 | 715 | 658 | |
| Water | 0 | −130 | −20 | +64 | +116 | +150 | +173 | +189 |
| | 80 | 492 | 468 | 445 | 423 | 406 | 392 | 382 |
| Glycerol | 25 | 437 | 407 | 380 | 352 | 327 | 308 | 294 |
| | 98·2 | 625 | 570 | 520 | 475 | 441 | | |
| Castor oil | 0 | 785 | 700 | 628 | 564 | 507 | 468 | 448 |

times, and glycerol four times, smaller. For comparison, the value for water (Pushin and Grebenshchikov, J., 1923, **123**, 2717) is also given in the tables. Of all the substances we have investigated, water has the smallest coefficient of adiabatic cooling.

With increasing pressure the value of $(dt/dp)_s$ decreases for all the substances investigated, so that the values of the function $(dt/dp)_s$ ultimately approach one another. This function has as yet been experimentally determined only for benzene at the ordinary temperature and a pressure of about 200 kg./cm.$^2$, Burton and Marshall (*Proc. Roy. Soc.*, 1891, **50**, 130) having found the value 0·0166. As the temperature coefficient of the function for benzene is unknown, their value cannot be compared with ours.

The curves for phenol, *p*-toluidine, and their mixtures show that the addition of 25 mol. per cent. (27·5 per cent. by weight) of *p*-toluidine increases very slightly, and at high pressures even decreases, the value of $(dt/dp)_s$ for phenol, although the value for the coefficient of adiabatic cooling for *p*-toluidine is considerably greater than for phenol. It is probable that this phenomenon is due to formation of the phenolate of *p*-toluidine, the existence of which has been proved by thermal analysis.*

* The results will be published separately. See also Philip, J., 1903, **83**, 828.

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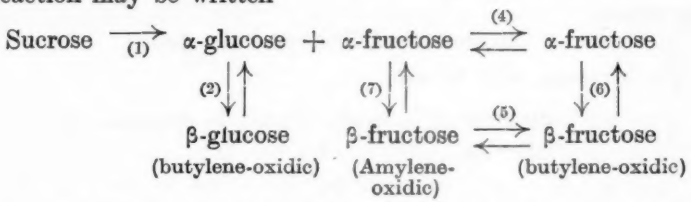
# CCLXIX.—*The Mutarotation Lag in Sucrose Inversion.*

By STUART WORTLEY PENNYCUICK.

THE inversion process is accepted as an exceedingly complex change, in which the monosaccharides are subject to structural and stereochemical rearrangements. Although finality has not been reached, the reaction may be written




(Haworth and Law, J., 1916, **109**, 1314; Haworth and Linnell, J., 1923, **123**, 294).

The polarimetric method of following the inversion involves the fundamental assumption that at any time, $t$, the concentration of sucrose is strictly proportional to $\lambda_t - \lambda_\infty$, where $\lambda$ represents the optical rotation. As all the above substances are optically active, this proportionality can only be strictly true when the equilibria marked 2, 4, 5, 6, and 7 are instantaneous, but it can be approximately true when the velocity coefficients of these equilibria are large compared with that of action (1).

In the presence of invertase, $k_1$ is generally large, whilst $k_2$ and $k_6$ have practically their minimum values (Hudson, *J. Amer. Chem. Soc.*, 1908, **30**, 1564), so that an appreciable mutarotational lag would be expected, and $k_1$ would no longer be obtainable from the simple logarithmic formula $1/t \,.\, \log(\lambda_0 - \lambda_\infty)/(\lambda_t - \lambda_\infty)$. The existence of such a mutarotational lag was first shown experimentally by O'Sullivan and Thomson (J., 1890, **57**, 834), who found that on "killing" the invertase with alkali at any time there was a "residual decrease" in the rotation of the solution. It has therefore been the practice when following this inversion, to remove samples from time to time, destroy the invertase with alkali and thus bring about the mutarotation equilibria, and then take the polarimetric reading. If this method be not followed, the results are considered open to question (Hudson, *loc. cit.*; Nelson and Vosburgh, *J. Amer. Chem. Soc.*, 1917, **39**, 790).

In presence of acids, however, $k_1$ may be relatively small, whilst the mutarotation coefficients, which also increase with the concentration of the catalyst, may be large. As these are the conditions for a small mutarotational lag, and as the unimolecular formula invariably gives "satisfactory" constants, it has been concluded

that in presence of acids the mutarotational lag is negligible. It is shown in this paper, both theoretically and experimentally, that the lag is not negligible; that $k_1$ is therefore not equal to $1/t \cdot \log(\lambda_0 - \lambda_\infty)/(\lambda_t - \lambda_\infty)$, but is given by the formula $k_1 = \frac{1}{t} \log \frac{Q + R + S}{(\lambda_t - \lambda_\infty)/A}$ where $A$ is the initial molecular concentration of the sucrose, $Q$ has the value $(\lambda_0 - \lambda_\infty)/A$, and $R$ and $S$ are the lag constants for the action.

*Mathematical Theory of the Action.*

The inversion may be written—

$$\begin{array}{ccc} \text{Sucrose} & \xrightarrow{(1)} & \alpha\text{-glucose } (y) + \text{fructose } (x) \\ (A - x) & & \\ & \overset{(2)}{\downarrow}\uparrow_{(3)} & \\ & \beta\text{-glucose } (x - y) & \end{array}$$

where the secondary changes in the fructose are provisionally neglected for mathematical convenience and for reasons that will develop later. The concentrations (gm.-mols./litre) are represented by the symbols above, $A$ being the initial sucrose concentration, $x$ the amount inverted in time $t$, and $y$ the concentration of α-glucose at time $t$. Of these three consecutive actions, (2) and (3) are opposed stereochemical changes, while (1) is a simple hydrolysis. Each is a unimolecular action, (1) being pseudo-unimolecular (the water having practically constant concentration), while (2) and (3) are strictly unimolecular (Nelson and Beegle, *J. Amer. Chem. Soc.*, 1919, **41**, 559). The velocity of hydrolysis is given by

(1) $\qquad dx/dt = k_1 (A - x),$

and the velocity of formation of α-glucose by

(2) $\qquad dy/dt = k_1 (A - x) - k_2 y + k_3 (x - y).$

Integration of (1) gives (when $t = 0$, $x = 0$)

(1a) $\qquad x/A = 1 - e^{-k_1 t}.$

Substituting this value of $x$ in (2) and integrating, we have (when $t = 0$, $y = 0$)

$$\frac{y}{A} = \frac{k_3}{k_2 + k_3}\{1 - e^{-(k_2 + k_3)t}\} - \frac{k_3 - k_1}{k_2 + k_3 - k_1}\{e^{-k_1 t} - e^{-(k_2 + k_3)t}\}.$$

By rearrangement this can be made to assume the form

$$(2a)\ \frac{y}{A} = \frac{k_3}{k_2 + k_3}(1 - e^{-k_1 t}) + \frac{k_1 k_2}{(k_2 + k_3)(k_2 + k_3 - k_1)}\{e^{-k_1 t} - e^{-(k_2 + k_3)t}\}.$$

By combining (1a) and (2a) we have

$$(3)\ \frac{x - y}{A} = \frac{k_2}{k_2 + k_3}(1 - e^{-k_1 t}) - \frac{k_1 k_2}{(k_2 + k_3)(k_2 + k_3 - k_1)}\{e^{-k_1 t} - e^{(k_2 + k_3)t}\}.$$

These settings of equations (2a) and (3) are specially instructive for the purpose in hand, as they show at a glance the effects of "lag." For, if α-glucose and β-glucose were always in equilibrium, their respective concentrations would be $y/A = k_3/(k_2 + k_3) \cdot (1 - e^{-k_1 t})$ and $(x - y)/A = k_2/(k_2 + k_3) \cdot (1 - e^{-k_1 t})$.

But the equations (2a) and (3) show that the actual proportional concentration of α-glucose, $(y/A)$, exceeds that value, while that of β-glucose, $(x - y)/A$, falls short of it by the amount

$$\frac{k_1 k_2}{(k_2 + k_3)(k_2 + k_3 - k_1)} \{e^{-k_1 t} - e^{-(k_2 + k_3)t}\}.$$

This quantity, then, is the exact measure of the effect due to a lag in the establishment of the glucose equilibrium. It stands good whether or not there be also a fructose complication, as the glucose and fructose interact neither with one another nor with the residual sucrose.

*The Course of the Glucose Lag and its Value.*—Since $e^{-k_1 t}$ and $e^{-(k_2 + k_3)t}$ both equal 1 when $t = 0$, and both equal 0 when $t = \infty$, the initial and the final values of the glucose lag are both 0; but somewhere between it must reach a maximum value. Suppose this occurs at time $t_m$. The maximum lag can occur only when $d\{e^{-k_1 t} - e^{-(k_2 + k_3)t}\}\ dt = 0$ or $de^{-k_1 t}/dt = de^{-(k_2 + k_3)t}/dt$, *i.e.*, when $k_1 e^{-k_1 t} = (k_2 + k_3) e^{-(k_2 + k_3)t}$.

This gives $$t_m = \frac{1}{k_2 + k_3 - k_1} \log_e \left(\frac{k_2 + k_3}{k_1}\right).$$

And the maximum lag/$A$ (at $t_m$) is then equal to

$$\frac{k_1 k_2}{(k_2 + k_3)(k_2 + k_3 - k_1)} (e^{-k_1 t_m} - e^{-(k_2 + k_3)t_m}) = \frac{k_1 k_2}{(k_2 + k_3)^2} e^{-k_1 t_m}$$

$$\text{or } \frac{k_2}{(k_2 + k_3)} e^{-(k_2 + k_3)t_m}.$$

The lag value at any other time is obviously calculable in terms of $t$ and the constants $A$, $k_1$, $k_2$, and $k_3$; and as these constants are known over quite a large range it will be convenient to see whether the lag is of measurable magnitude. From the nature of the glucose equilibrium, experimental study of the mutarotation can give only the sum of the velocity constants $k_2$ and $k_3$ (Hudson, *Z. physikal. Chem.*, 1903, **44**, 487). But the specific rotations of α-, β-, and α ⇄ β-glucose have been carefully determined by Nelson and Beegle (*loc. cit.*) as 111·2°, 17·5°, and 52·5°, respectively; and have been shown to be independent of temperature and concentration. It thus follows that at equilibrium we have 37·4 per cent. of α-glucose ⇄ 62·6 per cent. of β-glucose and therefore $k_2/k_3 = 1{\cdot}67$.

This ratio will give the individual values of $k_2$ and $k_3$ when their sum has been experimentally obtained.

Now the magnitude of the lag depends on the relative values of $k_1$ and $k_2 + k_3$; and further, the ratio $k_1/(k_2 + k_3)$ varies with the concentration of the acid catalyst, increasing from approximately $0{\cdot}4 \times 10^{-3}$ for a 0·001*N*-hydrochloric acid solution to about $0{\cdot}1 \times 10^{-1}$ for a 0·1*N*-solution. Very weak acid solutions, then, will show a minimum lag, while solutions in the neighbourhood of 0·1*N* (and perhaps also stronger acid solutions) will show the greatest lag.

The foregoing deductions may be applied to the case of a 17·1 per cent. ($A = 0{\cdot}5$) sucrose solution inverted by 0·1*N*-hydrochloric acid at 35°. The value of $k_1$ (from Table IIA) is $0{\cdot}00162 \times 2{\cdot}303 = 0{\cdot}00373$. (All constants in the following tables are calculated from the more usual $\log_{10}$ formula.) The value of $k_2 + k_3$ for the corresponding 9 per cent. glucose solution can be taken from Nelson and Beegle's figures (*loc. cit.*) as approximately 0·270, an approximate value being quite sufficient. On combining this value with the ratio $k_2/k_3 = 1{\cdot}67$, we have $k_2 = 0{\cdot}169$ and $k_3 = 0{\cdot}101$.

Using these values for $k_1$, $k_2$, and $k_3$, Table I has been set out.

TABLE I.

17·1 *per cent. Sucrose* + 0·1*N*-HCl *at* 35°.

| $t$ (mins.). | $\frac{x-y}{y}$. | $\frac{x}{A}$. | Lag $\frac{}{A} \times 10^4$. | Lag in degrees per gm.-mol. | $t$ (mins.). | $\frac{x-y}{y}$. | $\frac{x}{A}$. | Lag $\frac{}{A} \times 10^4$. | Lag in degrees per gm.-mol. |
|---|---|---|---|---|---|---|---|---|---|
| 0 | — | — | 0 | 0 | 80 | 1·49 | 0·257 | 65 | 0·22 |
| 2 | 0·16 | 0·0074 | 36 | 0·12 | 120 | 1·56 | 0·361 | 56 | 0·19 |
| 6 | 0·46 | 0·0222 | 68 | 0·23 | 240 | 1·63 | 0·592 | 36 | 0·12 |
| 10 | 0·69 | 0·0366 | 80 | 0·27 | 300 | 1·64 | 0·673 | 29 | 0·10 |
| 16·08 | 0·94 | 0·058 | 82 | 0·28 | 600 | 1·67 | 0·893 | 9·4 | 0·03 |
| 20 | 1·05 | 0·0719 | 81 | 0·27 | 1000 | 1·67 | 0·976 | 2·1 | 0·01 |
| 30 | 1·23 | 0·106 | 78 | 0·26 | ∞ | 1·67 | 1·000 | — | 0·00 |
| 60 | 1·44 | 0·201 | 70 | 0·24 | | | | | |

Column 2 sets out the ratio β-*glucose* : α-*glucose* at any time during the inversion. If there were no lag, this ratio would have the constant value of 1·67. The small values in the earlier part of the action are rather striking. Column 3 gives the fraction of the sucrose hydrolysed at any time. Column 4 gives the lag per gram-mol. As demanded by the theory, the lag passes through a maximum, at $t = 16{\cdot}08$ mins., $\left(t_m = \frac{1}{k_2 + k_3 - k_1} \log_e \left(\frac{k_2 + k_3}{k_1}\right)\right.$, *i.e.*, at a comparatively early stage in the action, when only 5·8 per cent. of the sucrose has been inverted. Column 5 gives the glucose lag in degrees (in a 2-dcm. tube) per gram-mol. of sucrose per litre, using the values of the specific rotations already given. The lag, though small, is quite appreciable, and $k_1$ obtained from $1/t \,.\, \log (\lambda_0 - \lambda_\infty)/(\lambda_t - \lambda_\infty)$ will not be a true measure of the hydrolysis constant, particularly in the earlier stages of the action.

It can now be said that whenever $k_2 + k_3$ greatly exceeds $k_1$ (as it generally does) the maximum lag is small and is reached and passed quite early, after which it slowly decreases, but will become nil only when no sucrose remains. Another consequence of the relatively large value of $k_2 + k_3$ as compared with $k_1$ is that $e^{-(k_2+k_3)t}$ must become sensibly nil and therefore quite negligible while $e^{-k_1 t}$ has still the value of a large fraction of unity, *i.e.*, while residual sucrose is still large or not long after the start of the action; and therefore the whole lag will be $\frac{k_1 k_2 A}{(k_2+k_3)(k_2+k_3-k_1)} e^{-k_1 t}$, that is, it will appear strictly proportional to the residual sucrose. From a consideration of the figures, it can be shown that at 20 mins. the error involved in neglecting $e^{-(k_2+k_3)t}$ in computing the lag would be about 0·5 per cent., while at 30 mins. it would be about 0·033 per cent. and practically beyond detection.

*The Polarimetric Method.*

Let the molar rotations (under the experimental conditions) of sucrose, fructose, α-glucose, and β-glucose be represented respectively by $\sigma$, $\phi$, $\alpha$, and $\beta$. Then the value for the solution will be

$$\frac{\lambda_t}{A} = \sigma e^{-k_1 t} - \phi(1 - e^{-k_1 t}) + \alpha \frac{k_3}{k_2+k_3}(1 - e^{-k_1 t}) + \beta \frac{k_2}{k_2+k_3}(1 - e^{-k_1 t}) + (\alpha - \beta) \frac{k_1 k_2}{(k_2+k_3)(k_2+k_3-k_1)} \{e^{-k_1 t} - e^{-(k_2+k_3)t}\}$$

and the lag effect is represented by the last term.

Re-arranging, we have

$$\frac{\lambda_t}{A} = \left(\alpha \frac{k_3}{k_2+k_3} + \beta \frac{k_2}{k_2+k_3} - \phi\right) + \left\{\left(\sigma + \phi - \alpha \frac{k_3}{k_2+k_3} - \beta \frac{k_2}{k_2+k_3}\right) + (\alpha - \beta) \frac{k_1 k_2}{(k_2+k_3)(k_2+k_3-k_1)}\right\} e^{-k_1 t} - \left\{(\alpha - \beta) \frac{k_1 k_2}{(k_2+k_3)(k_2+k_3-k_1)}\right\} e^{-(k_2+k_3)t}.$$

Or $$\lambda_t / A = P + (Q + R)e^{-k_1 t} - Re^{-(k_2+k_3)t}$$

where $P$, $Q$, and $R$ are constants.

Hence $$\lambda_0 / A = P + Q \text{ and } \lambda_\infty / A = P,$$

and thus $$(\lambda_0 - \lambda_\infty)/A = Q$$

and $$(\lambda_t - \lambda_\infty)/A = (Q + R)e^{-k_1 t} - Re^{-(k_2+k_3)t}$$

until, when $e^{-(k_2+k_3)t}$ becomes nil,

$$(\lambda_t - \lambda_\infty)/A = (Q + R)e^{-k_1 t}.$$

*The Graph of Log* $(\lambda_t - \lambda_\infty)/A$ *against* $t$.—The initial stages of the inversion cannot be followed experimentally and therefore it is the

usual practice to plot $\log (\lambda_t - \lambda_\infty)/A$ against $t$ and extrapolate to $t = 0$ and thus obtain $\log (\lambda_0 - \lambda_\infty)/A$. The formula $k_1 = 1/t \cdot \log (\lambda_0 - \lambda_\infty)/(\lambda_t - \lambda_\infty)$ is then applied (Rosanoff, Clark, and Sibley, *J. Amer. Chem. Soc.*, 1911, **33**, 1911).

It follows necessarily from the foregoing that on plotting $\log (\lambda_t - \lambda_\infty)/A$ against $t$, a curve will be obtained starting from $\log Q$ at $t = 0$, which must become rectilinear as soon as (but not before) $Re^{-(k_2+k_3)t}$ is negligibly small. This, as a fact, is soon after 20 minutes in the 0·1*N*-hydrochloric acid tests. Further, this straight line must extrapolate backwards to $\log (Q + R)$, and not to $\log Q$, at $t = 0$; and the equation for it is

$$\log_e (Q + R) - \log_e (\lambda_t - \lambda_\infty)/A = k_1 t$$

or

$$k_1 = 2{\cdot}303 \frac{1}{t} \log \frac{Q + R}{(\lambda_t - \lambda_\infty)/A}.$$

This should give a correct measure of $k_1$, which is simply the slope of the straight line.

We have therefore the important result that the curve obtained by plotting $\log (\lambda_t - \lambda_\infty)/A$ (with lag) against $t$ becomes rectilinear very early in the action, and is thereafter strictly parallel to the graph of $\log (\lambda_t - \lambda_\infty)/A$ (in total absence of lag) against $t$. The latter straight line starts from the true $\log (\lambda_0 - \lambda_\infty)/A$, but the former (with lag) straight line extrapolates backwards to a false starting point, $\log \left\{\frac{\lambda_0 - \lambda_\infty}{A} + R\right\}$, which, however, is the correct initial value for use with the preceding " with lag " formula. The slope of either straight line is then the correct measure of $k_1$.

*The Value of the Glucose Lag Constant.*—The actual lag at any point of the curve is given by

$$\frac{(\alpha - \beta)k_1 k_2 A}{(k_2 + k_3)(k_2 + k_3 - k_1)}(e^{-k_1 t} - e^{-(k_2+k_3)t})$$

or

$$RA(e^{-k_1 t} - e^{-(k_2+k_3)t})$$

where $R$ is the lag constant. Since all the contributory constants are known with, at any rate, approximate accuracy, $R$ may be calculated from them. Using the values of $\alpha$, $\beta$, $k_1$, $k_2$, and $k_3$ already given, $R$ (for 0·1*N*-hydrochloric acid at 35°) is equal to 0·296.

*The Fructose Lag.*—There is much evidence that the fructose mutarotation is complicated by a structural change (Haworth and Linnell, *loc. cit.*), but the fructose lag and the fructose lag constant cannot be evaluated owing to lack of data regarding " $\alpha$ "-fructose. Since, under comparable conditions, $k_4 + k_5$ for fructose is always

greater than $k_2 + k_3$ for glucose (Nelson and Beegle, *loc. cit.*), the fructose lag is doubtless smaller than the glucose lag.

## EXPERIMENTAL.

The usual polarimetric method cannot give an experimental value of $\lambda_0$, nor does it generally give any values over the first 10 to 20 minutes of the inversion. If "$\lambda_0$" is obtained by extrapolating $\log(\lambda_t - \lambda_\infty) = A + Bt$ to $t = 0$, or if the short time interval formula $k_1 = 1/(t_2 - t_1) \cdot \log(\lambda_{t1} - \lambda_\infty)/(\lambda_{t2} - \lambda_\infty)$ is used, it is evident from the foregoing that a satisfactory (and correct) $k_1$ may be obtained, and yet the mutarotational lag may be appreciable. Or if the graph of $\lambda$ against $t$ is extrapolated to $t = 0$ (as is sometimes the case), too large a value of "$\lambda_0$" is again obtained and the lag is effectively hidden; this is due to the fact that the lag rapidly passes through a maximum and is then strictly proportional to remaining sucrose.

It is essential, then, to devise some method of following the action polarimetrically which admits of a direct determination of $\lambda_0$, and it would be preferable if the action could be followed both before and after the mutarotation equilibria are set up. A very slow inversion would allow an approximate experimental determination of $\lambda_0$, but an examination of the relative values of $k_1$ and $k_2 + k_3$ for slow inversions (whether weak-acid or low-temperature actions) shows that the lag in all such cases has a value which would be difficult to detect experimentally.

The method developed and applied was essentially as follows. Weighed quantities of acid and of sugar solutions were mixed at the temperature of the experiment, the inversion was allowed to proceed in the reaction bottle in a water-bath, and samples were withdrawn from time to time. Each sample was immediately and rapidly chilled to 0° and the inversion thus stopped. The rotation was then read in a specially prepared 2-dcm. tube in an ice-boat, and as the mutarotational equilibria were incomplete the values of $\lambda_t - \lambda_\infty$ with lag were obtained.

Then a fresh reaction was run, measured samples were removed from time to time, "killed" with sodium hydroxide, chilled to 0°, and the rotation read. As the equilibria were now complete, $\lambda_t - \lambda_\infty$ without lag was obtained.

These will be called Method I and Method II respectively.

*Method I.* This method possesses some outstanding advantages. First, the temperature control may be made far more efficient than when a jacketed polarimeter tube and a circulating water supply are used. Secondly, the reaction is so slowed down on chilling—in dilute acids practically stopped—that a very accurate

reading can be taken of the rotation corresponding to any time. With the ordinary method the reading of the rotation during the running reaction involves a relatively large experimental error, particularly in the early stages, or when stronger acids are used. Thirdly (and chiefly) by cooling the necessary weights of hydrochloric acid and sugar to 0°, mixing at this temperature, and immediately reading the rotation, the true value of $\lambda_0$ is obtained experimentally.

Further, the method allows of an extension; for, at 0°, although the inversion process is practically stopped dead, any incomplete mutarotations can steadily proceed, because of their relatively large velocities. Owing to the large difference in the values of the sucrose, fructose, and glucose velocity coefficients, the three reactions are practically sorted out at 0°, the inversion is stopped, the fructose mutarotation proceeds very rapidly to equilibrium, and the glucose mutarotation proceeds relatively slowly to equilibrium. It was hoped, then, by means of this extension to measure the greater part of the actual lag. The fructose lag is not only smaller than the glucose lag, but it suffers interference during the chilling of the solution, owing to a displacement of the fructose equilibrium with fall in temperature. The glucose, on the other hand, shows a more pronounced lag, and the specific rotations of α-, β-, and α ⇄ β-glucose are quite unaffected by a fall in temperature (Nelson and Beegle, *loc. cit.*). This convenient fact was made use of, and the lag measured by keeping each solution at 0° for 4, 8, or 24 hours, and retaking the rotation. The latter values gave $\lambda_t - \lambda_\infty$ after mutarotational equilibrium.

*Method II.*—The second method, which was quite independent of the first, measured the rotations after the inversion had been stopped with sodium hydroxide and after time had been allowed for mutarotational equilibria. It thus served as a check on the second readings in method I.

The same acid and sugar concentrations were used. At suitable time intervals a 50 c.c. sample was rapidly removed and run into a flask together with 10 c.c. of sodium hydroxide solution of five times the acid strength. The two pipettes delivered at the same rate and the streams were caused to mix; the time was taken when half the solution had been delivered. The mixtures were then chilled to 0°, put in the ice pack for 24 hours, and then read at 0° in the usual way.

Exact neutralisation of the acid—particularly strong acid—in this way is difficult, especially as there is a slight volume change during the inversion. If the solution is made slightly basic, the well-known alkali effect on the invert products may interfere with

the final equilibria. The solutions were therefore kept just on the acid side of neutral. It was found that 0·002*N*-hydrochloric acid at 0° would cause a fall of about 0·01° per 24 hours for a 17·1 per cent. sucrose solution. Therefore no solution was used of greater final acid concentration than this, and very few even of this concentration.

The times taken to attain mutarotational equilibrium are practically the same for these different (and weak) acid solutions, owing to the glucose and fructose mutarotational constants in weak acid solutions being reasonably constant over a wide $p_H$ range (Nelson and Beegle, *loc. cit.*). The acid strength of the "neutralised" solution is then immaterial, provided that it is never greater than 0·002*N*.

The time required to attain equilibrium was obtained by reading many of the solutions (over the whole range of inversion), 24 hours, 48 hours, and 120 hours after chilling. No change greater than the experimental error was found after 24 hours. All solutions were then kept for at least 24 hours before reading.

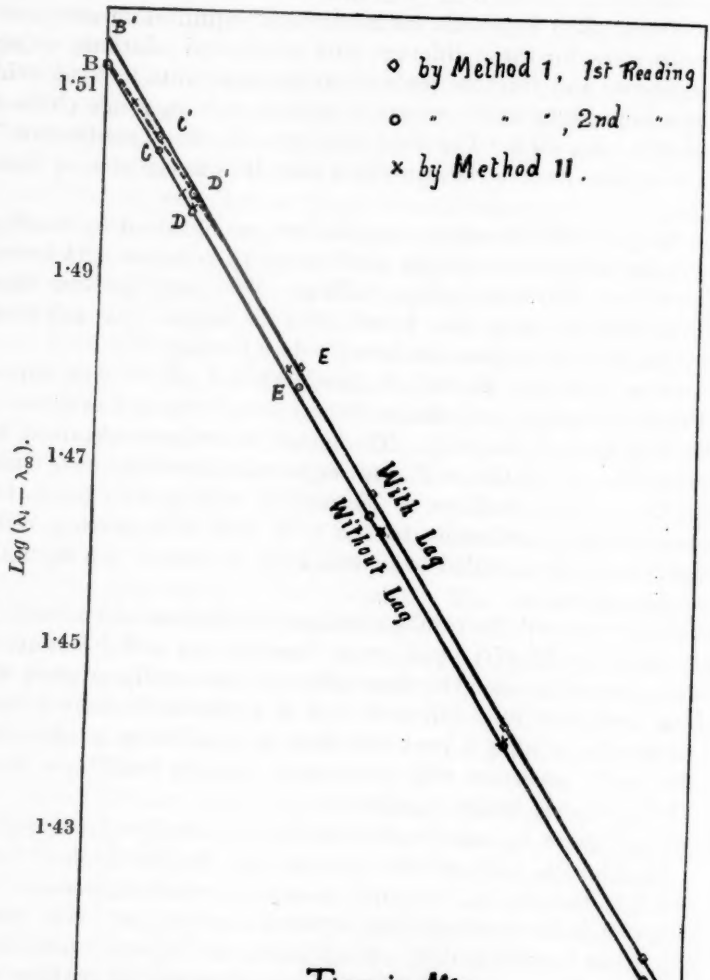
It can be seen that Method II, like Method I, allows an accurate polarimetric reading, and also an experimental determination of $\lambda_0$ (Fales and Morrell, *loc. cit.*). The latter was always obtained by weighing 25 c.c. of the acid and sugar solutions into two flasks (using the weight check as in Method I), adding 10 c.c. of the standard sodium hydroxide to the acid, and then mixing. The solutions were then chilled to 0° and held as above. An accurate $\lambda_0$ was aimed at.

Table IIA sets out the results obtained by Method I for a 0·099*N*-hydrochloric acid–17·1 per cent. sucrose ($A = 0{\cdot}5$) solution. Columns 3 and 5 show the time intervals after chilling when the readings recorded in columns 4 and 6 respectively were taken. The figures in column 6 were obtained after allowing a correction for the slight inversion still proceeding, namely 0·027° per hour per 17·1 per cent. initial sucrose.

Column 8 gives $k_1$, calculated from the formula $k_1 = 1/t \,.\, \log\{Q + (R + S)\}/\{(\lambda_t - \lambda_\infty)/A\}$, where $\lambda_t - \lambda_\infty$ with lag is obtained from column 4, $Q$, that is, $(\lambda_0 - \lambda_\infty)/A$, is experimentally determined as 32·53, and $S$ is the corresponding fructose lag constant. The value of $R + S$ can be obtained by extrapolating the log curve (with lag) as shown in Fig. 1, but a better value is obtained by making use of the average $\log \dfrac{\lambda_t - \lambda_\infty \text{ (with lag)}}{\lambda_t - \lambda_\infty \text{ (without lag)}}$ (0·0020), shown in column 7. On using this, $R + S$ has the value 0·30, and $\lambda_0 - \lambda_\infty + A(R + S)$ is therefore 32·65. This is approximately the same as the value obtained by extrapolation in Fig. 1, and $k_1$ is then calculated from

$\frac{1}{t}\log\frac{32{\cdot}65}{\lambda_t-\lambda_\infty\ \text{(with lag)}}$. Column 9 gives the values of $k_1$ obtained from $\frac{1}{t}\log\frac{\lambda_0-\lambda_\infty}{\lambda_t-\lambda_\infty\ \text{(no lag)}}$ where $\lambda_0-\lambda_\infty$ is the true starting point

FIG. 1 (0·099 *N*-HCl).




and is experimentally determined as 32·53°, and $\lambda_t-\lambda_\infty$ (without lag) is given by column 6. The $k_1$ constants (with and without lag) agree within the limits of experimental error.

TABLE IIA (*Method I*).

0·099*N*-HCl + 17·1% *Sucrose at* 35°.

| $t$ (mins.). | % of initial sucrose. | Hrs. later. | $\lambda_t - \lambda_\infty$ (with lag). | Hrs. later. | $\lambda_t - \lambda_\infty$ (without lag). | $\log \frac{\lambda_t - \lambda_\infty \text{ (with lag)}}{\lambda_t - \lambda_\infty \text{ (without lag)}}$ | $k_1 \times 10^4$ (with lag). | $k_1 \times 10^4$ (without lag). |
|---|---|---|---|---|---|---|---|---|
| | 100 | | (32·53) | 23·8 | 32·53 | | | |
| 5·97 | 98·0 | 0·51 | 31·94 | 23·8 | 31·85 | 0·0013 | (1660) | 1540 |
| 9·82 | 96·5 | 0·54 | 31·51 | 23·9 | 31·38 | 0·0018 | 1620 | 1600 |
| 21·77 | 92·6 | 0·57 | 30·22 | 23·9 | 30·08 | 0·0021 | 1560 | 1570 |
| 29·80 | 89·8 | 0·49 | 29·33 | 23·9 | 29·20 | 0·0019 | 1580 | 1570 |
| 44·47 | 85·1 | 0·54 | 27·75 | 24·0 | 27·64 | 0·0016 | 1597 | 1592 |
| 59·60 | 80·3 | 0·51 | 26·25 | 24·0 | 26·15 | 0·0016 | 1597 | 1591 |
| 79·60 | 74·6 | 0·50 | 24·34 | 24·0 | 24·26 | 0·0014 | 1608 | 1601 |
| 93·18 | 71·0 | 0·54 | 23·14 | 23·6 | 23·08 | 0·0012 | 1609 | 1600 |
| 119·60 | 64·5 | 0·52 | 21·03 | 23·6 | 20·95 | 0·0016 | 1601 | 1599 |
| 142·9 | 59·1 | 0·52 | 19·28 | 23·7 | 19·22 | 0·0014 | 1604 | 1600 |
| 179·7 | 51·6 | 0·54 | 16·87 | 22·7 | 16·72 | 0·0039 | 1600 | 1610 |
| 239·8 | 41·1 | 0·52 | 13·45 | 22·0 | 13·37 | 0·0026 | 1608 | 1610 |
| 299·8 | 32·8 | 0·53 | 10·72 | 22·7 | 10·67 | 0·0020 | 1614 | 1614 |
| 359·7 | 26·1 | 0·51 | 8·52 | 26·0 | 8·49 | 0·0015 | 1623 | 1624 |
| 522·9 | 14·1 | 0·52 | 4·62 | 27·1 | 4·59 | 0·0024 | 1626 | 1627 |
| 589·4 | 11·1 | 0·47 | 3·63 | 28·3 | 3·61 | 0·0024 | 1619 | 1620 |
| 639·8 | 9·1 | 0·52 | 3·00 | 22·0 | 2·95 | (0·0073) | 1621 | 1628 |
| | 0 | | | | Average | 0·0020 | | |

Lag constant $R$ (calculated) = 0·30; (found) = 0·30.

Table IIB sets out the results obtained by Method II for an inversion in a solution of the same acid-sugar strength as in Method I. There is no lag by this method and $k_1$ is obtained from the ordinary direct formula. The values of $\lambda_t - \lambda_\infty$ have all been multiplied by 6/5 (approx.) to correct for the volume change on neutralisation, so that they may be compared graphically with those from Method I. The "constant" is in satisfactory agreement with those shown in Table IIA. The gradual increase will be commented on later.

TABLE IIB (*Method II*).

0·099*N*-HCl + 17·1 % *Sucrose at* 35°.

| $t$ (mins.). | % Sucrose. | Hrs. later. | $\lambda - \lambda_\infty$ (without lag). | $k_1 \times 10^6$ (without lag). | $t$ (mins.). | % Sucrose. | Hrs. later. | $\lambda_t - \lambda_\infty$ (without lag). | $k_1 \times 10^6$ (without lag). |
|---|---|---|---|---|---|---|---|---|---|
| — | 100 | — | 32·53 | — | 96·17 | 70·2 | 48 | 22·88 | 1591 |
| 2·72 | 99·1 | 48 | 32·22 | 1490 | 128·1 | 62·4 | 48 | 20·32 | 1597 |
| 5·80 | 98·0 | 48 | 31·86 | 1540 | 187·27 | 50·1 | 48 | 16·29 | 1603 |
| 8·70 | 96·9 | 49 | 31·54 | 1540 | 251·7 | 39·4 | 48 | 12·80 | 1609 |
| 9·92 | 96·5 | 48 | 31·39 | 1550 | 288·75 | 34·2 | 48 | 11·16 | 1609 |
| 20·48 | 92·8 | 48 | 30·20 | 1578 | 385·0 | 23·8 | 48 | 7·76 | 1617 |
| 30·75 | 89·4 | 49 | 29·10 | 1578 | 628·9 | 9·6 | 45 | 3·14 | 1615 |
| 44·83 | 84·9 | 50 | 27·63 | 1584 | 660·2 | 8·5 | 44 | 2·78 | 1620 |
| 60·58 | 80·1 | 51 | 26·06 | 1590 | | 0 | — | 0 | |

Table III shows the values of the mutarotational lag for 17·1 per cent. sugar and acid strengths 0·02, 0·099, 0·507 and 0·905 *N*-hydro-

chloric acid. With stronger acids the lag cannot be calculated, as $k_2 + k_3$ is really too large for actual measurement. Where the lag can be calculated, there is good agreement with the lag experimentally found. This cannot be interpreted as meaning that the fructose lag is inappreciable, for owing to the experimental demands the whole of the glucose lag cannot be picked up. It seems indirectly to indicate that the fructose lag is small.

The lag constants and inversion coefficients are also set out.

Figs. 1 and 2 show the graph of log $(\lambda_t - \lambda_\infty)$ against time, for the 0·02 and 0·099 *N*-hydrochloric acid solutions, over the initial stages (approx. 20 per cent.) of the inversion.

TABLE III.

17·1 % *Sugar.*

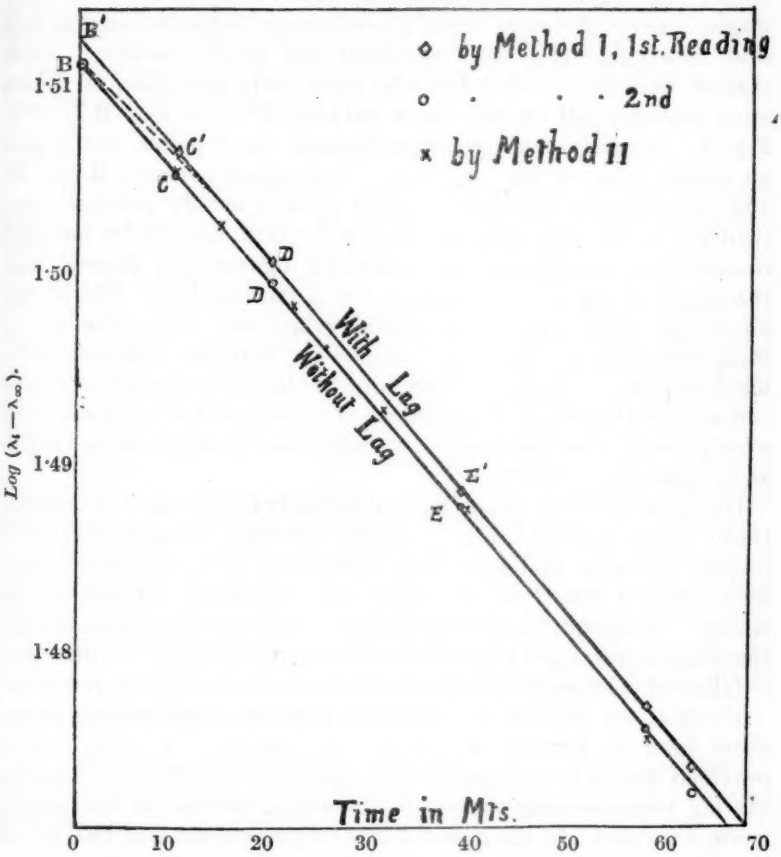
| % of initial sucrose remaining. | 0·02*N*-HCl at 40°. Lag found. | Lag cal. | 0·099*N*-HCl at 35°. Lag found. | Lag cal. | 0·507*N*-HCl at 35°. Lag found. | 0·905*N*-HCl at 35°. Lag found. |
|---|---|---|---|---|---|---|
| 100 | — | 0·00 | — | 0·00 | — | — |
| 99 | 0·08 | 0·08 | — | 0·09 | — | — |
| 98 | 0·10 | 0·09 | 0·09 | 0·11 | — | — |
| 97 | 0·09 | 0·09 | 0·12 | 0·13 | 0·10 | — |
| 95 | 0·07 | 0·10 | 0·15 | 0·14 | 0·12 | 0·10 |
| 92 | 0·08 | 0·09 | — | — | 0·12 | 0·07 |
| 90 | 0·09 | 0·09 | 0·14 | 0·13 | — | 0·11 |
| 85 | 0·10 | 0·09 | 0·10 | 0·13 | 0·10 | — |
| 70 | 0·09 | 0·07 | 0·06 | 0·10 | 0·10 | — |
| 60 | 0·05 | 0·06 | 0·05 | 0·08 | 0·09 | 0·07 |
| 50 | 0·06 | 0·05 | 0·12 | 0·07 | 0·08 | 0·09 |
| 40 | 0·07 | 0·04 | 0·08 | 0·06 | 0·07 | 0·07 |
| 30 | 0·04 | 0·03 | 0·05 | 0·05 | 0·06 | 0·04 |
| 20 | 0·02 | 0·03 | 0·01 | 0·03 | 0·02 | 0·02 |
| 10 | 0·03 | 0·01 | 0·01 | 0·02 | 0·01 | 0·02 |
| Lag constant | 0·20 | 0·197 | 0·30 | 0·30 | 0·32 | 0·28 |
| $k_1$ (inversion) | 0·000603 | | 0·00162 | | 0·0102 | 0·0224 |
| Time to max. lag. | 31·6 mins. | | 16·08 mins. | | | |
| Average Log $\frac{\lambda_t - \lambda_\infty \text{ (Lag)}}{\lambda_t - \lambda_\infty \text{ (No lag)}}$ | 0·0013 | | 0·0020 | | 0·0021 | 0·0018 |

*Discussion and Conclusion.*

The results uphold the theoretical conclusions. Figs. 1 and 2 are especially instructive. B is the true starting point of the action and the B C D E curve (without lag) is rectilinear and of slope $k_1$. The B $C^1$ $D^1$ $E^1$ curve (with lag) becomes rectilinear at some early time and is thereafter parallel to the B C D E straight line, and its slope is also $k_1$. Either straight line (and therefore any method that gives either straight line) can thus give the correct value of $k_1$, the inversion constant. It is noticed that the usual (with lag) curve does not extrapolate back to the true log $(\lambda_0 - \lambda_\infty)$ as is generally supposed, but to log $\{\lambda_0 - \lambda_\infty + A(R + S)\}$, where

$R + S$ is the total lag constant. If the simple formula $k_1 \log (\lambda_0 - \lambda_\infty)/(\lambda_t - \lambda_\infty)$ be applied to the B $C^1$ $D^1$ $E^1$ (with lag) curve, $k_1$ cannot be constant, but will show a pronounced increase. But $k_1$ obtained from $1/t \,.\, \log \{\lambda_0 - \lambda_\infty + A(R + S)\}/(\lambda_t - \lambda_\infty)$, where $\lambda_0 - \lambda_\infty + A(R + S)$ is directly determined by experiment or by extrapolation, is the true unimolecular inversion constant.

FIG. 2 (0·02 *N*-HCl).




When invertase is the catalyst, the lag is generally much greater; even so, if the actual hydrolysis were unimolecular the foregoing indicates that it would still be possible to follow the inversion by the ordinary direct method without having to adopt the more tedious "neutralising" method. But, as Nelson and Vosburgh (*loc. cit.*) have shown quite definitely that the inversion without lag is not unimolecular, a theoretical treatment on the preceding lines

is not possible. As the mechanism of such heterogeneous actions is unknown, and is doubtless more or less complex, the mutarotational lag cannot be neglected in the experimental work.

Armstrong and Caldwell (*Proc. Roy. Soc.*, 1905, **74**, 195), in a well-known paper, show that in the case of weak acid catalysis (0·016*N*-hydrochloric acid approx., wrongly referred to as *N*/500) the inversion constant shows a pronounced increase over the first 40 per cent. of the action, and more particularly in the very early stages. They therefore draw a comparison between enzyme and acid catalysis. The mutarotational lag would, however, overshadow the effect looked for, and their early experimental points most probably fall on the curve between $B^1$ $C^1$ $D^1$ and B C D in Fig. 1. A careful extrapolation through these points would give an initial value of log "$\lambda_0 - \lambda_\infty$" somewhere between B and $B^1$ and the inversion coefficient would show a steady increase, particularly in the early stages. Rosanoff, Clark, and Sibley (*loc. cit.*) re-examined Armstrong and Caldwell's figures and showed that the graph of log $\lambda_t - \lambda_\infty$ against $t$ is a straight line. But it cuts above the very early experimental values and hence the use of their extrapolated "$\lambda_0 - \lambda_\infty$" causes the first few constants to be much too large. In fact, throughout the literature records are very common of abnormally large values of $k_1$ early in the inversion with slow actions; and these are not wholly due to experimental error, as is generally believed.

Owing to the above graph being invariably rectilinear it is assumed that "sugar hydrolysis is a simple reaction, unimolecular with respect to sugar and free from disturbing (*i.e.*, relatively slow) mutarotation reactions or other side reactions throughout its course" (Rosanoff, Clark, and Sibley). It is now seen that, though the graph is a straight line and the action unimolecular, the inversion as followed polarimetrically is not free from disturbing side reactions.

Further, the lag will not interfere with the applicability of the short interval formula $k_1 = 1/(t_2 - t_1) \cdot \log (\lambda_{t1} - \lambda_\infty)/(\lambda_{t2} - \lambda_\infty)$, provided that it is not applied very early in the action, *i.e.*, before the lag becomes proportional to remaining sucrose or the graphs become parallel. In the case of 0·099*N*-hydrochloric acid this would be after 20 mins., and for 0·02*N*-hydrochloric acid 35 mins.

The values of the lag experimentally found need little comment. They are recognised as minimum values, as are also the lag constants.

The steady increase of $k_1$ as the reaction proceeds (set out in Tables IIA and IIB) was general with all the inversions examined. It is most probably due to the change of thermodynamic environment (and the consequent increase of hydrogen-ion activity) caused by the liberation of two molecular sugar species for each one

hydrolysed, and the accompanying decrease in total water (about 1 per cent.).

*Experimental Detail.*—A high degree of accuracy was essential, and was kept in view throughout the work.

The sugar was purified according to Kraisy (*Z. Ver. deut. Zuckerind.*, 1921, 785), and a high grade Schmidt and Haensch polarimeter used.

Most of the reactions were run in two or three sets, and to obtain reproducible mixtures weighed quantities of acid and of sugar solution were mixed while immersed in the water-bath.

The solutions were chilled to 0° by running them through a spiral tube surrounded by crushed ice.

*Summary.*

1. It has been calculated from a knowledge of the inversion constant of sucrose and the mutarotation constants of glucose, that the mutarotational lag due to glucose is quite appreciable when acids catalyse the inversion.

2. It has been shown that after a brief time interval the lag becomes strictly proportional to the concentration of the remaining sucrose, with the result that the graph of log $(\lambda_t - \lambda_\infty)$ with lag and that of log $(\lambda_t - \lambda_\infty)$ without lag, against $t$, become strictly parallel, and both have the slope $k_1$, the inversion constant.

3. Methods have been developed for following the inversion before and after mutarotational equilibrium, and hence the total lag and the lag constant have been measured in several cases.

4. The usual method of following the inversion while the lag is present gives the correct value for $k_1$ if certain precautions are observed, but the curve log $(\lambda_t - \lambda_\infty)$ with lag against time does not extrapolate to log $(\lambda_0 - \lambda_\infty)$ at $t = 0$, but to log $\{\lambda_0 - \lambda_\infty + A(R + S)\}$, where $R + S$ is the total lag constant under the given conditions, $k_1$ being given by $\frac{1}{t} \log \frac{\lambda_0 - \lambda_\infty + A(R + S)}{\lambda_t - \lambda_\infty}$.

5. The short-interval formula also gives the correct $k_1$ (whether the lag is appreciable or not), so long as it is not applied in the very early stages of the inversion.

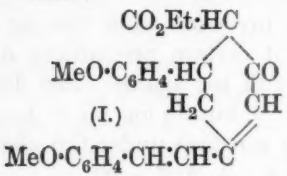
I am very much indebted to Professor Sir Orme Masson for some valuable criticism and suggestions, which have been made use of in the setting out of this paper. My thanks are also due to Mr. Winsor, B.Sc., and to Mr. Carter, B.Sc., for help in the experimental work.

THE UNIVERSITY OF ADELAIDE. [*Received, February 25th*, 1924.]

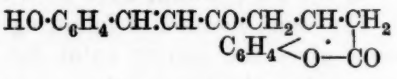
# CCLXX.—*The Interaction of Acetoacetic Ester and o-Hydroxydistyryl Ketones.*

By ISIDOR MORRIS HEILBRON and THOMAS ALFRED FORSTER.

In a previous communication (this vol., p. 340) an account was given of the products obtained from the condensation of acetoacetic ester with monostyryl ketones containing an *o*-hydroxyl group in the styryl residue and also with their methyl ethers. It was found that whereas the latter readily yielded *cyclo*hexenones, these substances were never obtained in the case of the free hydroxyketones, which formed either γ-pyrans or dihydrocoumarin derivatives. The study of this reaction has now been extended to 2 : 2′-dihydroxydistyryl ketone, its mono- and di-methyl ethers. The addition of acetoacetic ester to distyryl ketone itself was examined by Knoevenagel and Speyer (*Ber.*, 1902, **35**, 395), who showed that, in presence of diethylamine, ethyl distyryl ketone acetoacetate was first formed. Under the influence of either hydrogen chloride or 10 per cent. sodium hydroxide solution, this substance readily lost a molecule of water, yielding ethyl 3-phenyl-5-styryl-$\Delta^5$-*cyclo*hexen-1-one-2-carboxylate. 2 : 2′-Dimethoxydistyryl ketone behaves in a similar manner—ethyl 3-*o*-methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one-2-carboxylate (I) was directly obtained when the ketone was allowed to interact with acetoacetic ester in presence of 10 per cent. sodium hydroxide solution.

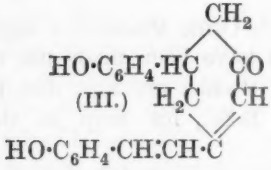


(I.)

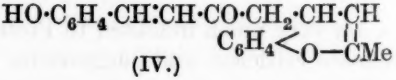


(II.)

With 2 : 2′-dihydroxydistyryl ketone, two compounds were isolated, a dihydrocoumarin derivative (II) and a compound of empirical formula $C_{20}H_{18}O_3$ which would correspond either to the *cyclo*hexenone (III) or the benzopyran (IV).



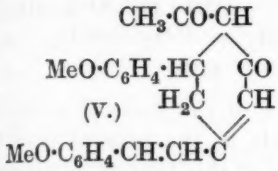
(III.)



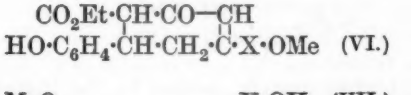
(IV.)

That the substance was probably a *cyclo*hexenone was indicated by the fact that it produced a deep red coloration with concentrated

sulphuric acid, a reaction indicative of *cyclo*hexenone formation (Borsche, *Annalen*, 1910, **375**, 145). Final proof was supplied by the fact that it yielded a dimethyl ether identical with the compound obtained by removal of the acetyl group from 2-acetyl-3-*o*-methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one (V).



(V.)

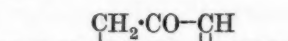


(VI.)

MeO . . . . X·OH (VII.)

(X·OMe and X·OH denote $CH{:}CH{\cdot}C_6H_4{\cdot}OMe$ and $CH{:}CH{\cdot}C_6H_4{\cdot}OH$, respectively.)

The interaction of 2′-methoxy-2-hydroxydistyryl ketone with acetoacetic ester resulted in the isolation of two products of empirical formulæ $C_{24}H_{24}O_5$ and $C_{21}H_{20}O_3$. The former compound on methylation produced a dimethyl ether identical with the *cyclo*hexenone (I), from which it follows that it must be represented as having the constitution VI or VII. In the case of the other compound, three possibilities (formulæ VIII, IX, and X) present themselves. That the substance was actually a *cyclo*hexenone was proved by the fact that, on methylation, a dimethyl ether identical with the dimethyl ether of (III) was obtained.



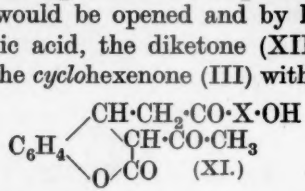
(VIII.)

(IX.) MeO . . . . X·OH

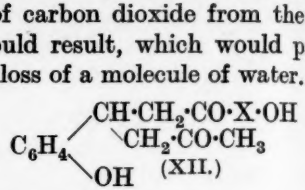
(X. = methyl ether of IV.)

It will be observed that whereas in the condensation of 2 : 2′-dihydroxydistyryl ketone with acetoacetic ester the carbethoxy-group is split off, with the corresponding dimethoxy-derivative, not only is this group not eliminated, but it is actually exceedingly difficult to remove. We therefore ascribe the constitution (VII) to the compound in which the carbethoxy-group is retained during the interaction of 2-hydroxy-2′-methoxydistyryl ketone with acetoacetic ester, the carbethoxy-free derivative being accordingly fixed as (VIII). Although the precise function of the *o*-hydroxyl group in bringing about the elimination of the carbethoxyl residue has not been absolutely determined, we consider that, in all cases where the addendum attaches itself to the styryl residue containing the *o*-hydroxyl group, a coumarin derivative first results through the elimination of a molecule of alcohol. Thus in the case of 2 : 2′-dihydroxydistyryl ketone, 3-acetyl-4-*o*-hydroxystyracyldihydrocoumarin (XI) would be formed, and the actual isolation of the

acetyl-free coumarin derivative (II) lends considerable weight to this assumption. In the presence of excess alkali, the coumarin ring would be opened and by loss of carbon dioxide from the β-ketonic acid, the diketone (XII) would result, which would pass into the *cyclo*hexenone (III) with the loss of a molecule of water.



(XI.)



(XII.)

Unfortunately, owing to the instability of the β-acetyl group in the coumarin ring, we have been unable in the present case to isolate the compound XI. The existence of this type of compound is clearly illustrated, however, by the formation of the analogously constituted 3-acetyl-4-phenacyldihydrocoumarin from 2-hydroxystyryl phenyl ketone and acetoacetic ester (Forster and Heilbron, *loc. cit.*). It will be noted that the diketone (XII) could readily react in the tautomeric enol form, and in this condition the formation of benzo-γ-pyrans would readily result, which reaction invariably occurs with the simple *o*-hydroxystyryl ketones. The preferential formation of *cyclo*hexenones from *o*-hydroxydistyryl ketone and its monomethyl ether may be attributed to the enormously enhanced reactivity of the carbonyl group when conjugated with an αβ-ethylenic linking.

## Experimental.

3-o-*Hydroxyphenyl*-5-o-*hydroxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one* (III).—A mixture of 2 : 2′-dihydroxydistyryl ketone (14 gms.; 1 mol.), ethyl acetoacetate (1·5 mols.), sodium hydroxide solution (12 c.c of 50%; 3 mols.), and sufficient water to maintain solution was kept at room temperature for 4 hours. The sodium salt of the *cyclo*hexenone usually separated completely, and was decomposed by dilute acetic acid at 0°. If no separation of salt occurred, dilute acetic acid was added direct to the solution. The more sparingly soluble 4-*o*-hydroxystyracyldihydrocoumarin separated first and the hexen-1-one was obtained from the filtrate on dilution with water. It crystallises from methyl alcohol in pale yellow prisms (yield 4 gms.), m. p. 240°, containing 1 mol. of methyl alcohol of crystallisation, which is removed slowly in the steam-oven. It develops a red coloration in concentrated sulphuric acid (Found: C = 74·7; H = 6·6. $C_{20}H_{18}O_3,CH_4O$ requires C = 74·3; H = 6·5%). Anhydrous compound (Found: C = 78·1; H = 6·0. $C_{20}H_{18}O_3$ requires C = 78·4; H = 5·9%).

4-o-*Hydroxystyracyldihydrocoumarin* (II) crystallises from dilute acetone in colourless crystals, m. p. 235°, and develops only a pale yellow coloration with concentrated sulphuric acid (yield 1·5 gms.).

(Found: C = 74·1; H = 5·2. $C_{19}H_{16}O_4$ requires C = 74·3; H = 5·1%). The *methyl ether* crystallises from light petroleum in colourless prisms, m. p. 130° (Found: C = 74·8; H = 5·6. $C_{20}H_{18}O_4$ requires C = 74·6; H = 5·6%).

3-o-*Methoxyphenyl*-5-o-*methoxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one* (I).—A mixture of the corresponding dihydroxy-*cyclo*hexenone (6 gms.), sodium hydroxide solution (20 c.c. of 10%), and acetone (60 c.c.) was warmed on a water-bath, and methyl sulphate (3 c.c.) added over a period of ½ hour. The dimethyl ether separated out on dilution. Feathery needles, m. p. 128°, from benzene–light petroleum (Found: C = 78·8; H = 6·6. $C_{22}H_{22}O_3$ requires C = 79·0; H = 6·6%).

2 : 2′-*Dimethoxydistyryl ketone*, prepared by methylation of 2 : 2′-dihydroxydistyryl ketone, crystallises from alcohol in yellow plates, m. p. 127°, only sparingly soluble in cold alcohol (Found: C = 77·5; H = 6·2. $C_{19}H_{18}O_3$ requires C = 77·6; H = 6·1%).

*Ethyl* 3-o-*Methoxyphenyl*-5-o-*methoxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one*-2-*carboxylate*.—A mixture of 2 : 2′-dimethoxydistyryl ketone (6 gms.), ethyl acetoacetate (4 c.c.), and boiling alcohol (70 c.c.) was treated with sodium hydroxide solution (8 c.c. of 10%). After 2 hours, the ester was filtered off and recrystallised from ligroin (yield 7 gms.); pale yellow needles, m. p. 159°, practically insoluble in alcohol, moderately soluble in hot ligroin, exceedingly soluble in benzene. The solution in concentrated sulphuric acid is carmine red. All attempts at removal of the carbethoxy-group with either acid or alkali proved fruitless (Found: C = 73·8; H = 6·5. $C_{25}H_{26}O_5$ requires C = 73·9; H = 6·4%).

3-o-*Hydroxyphenyl*-5-o-*methoxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one* (VIII).—A mixture of 2′-methoxy-2-hydroxydistyryl ketone (7 gms.; 1 mol.), ethyl acetoacetate (1½ mols.), boiling alcohol (20 c.c.), and sodium hydroxide solution (4 c.c. of 50%) was kept for 12 hours. The solid obtained was suspended in a large volume of water and decomposed by dilute acetic acid. The crude *cyclo*hexenone was crystallised first from absolute alcohol and then repeatedly from benzene–light petroleum; pale yellow needles, m. p. 172°, sparingly soluble in alcohol. The solution in aqueous sodium hydroxide is yellow, in concentrated sulphuric acid, carmine red. The *methyl ether* is identical with the dimethyl ether of III (Found: C = 78·3; H = 6·3. $C_{21}H_{20}O_3$ requires C = 78·7; H = 6·3%).

*Ethyl* 3-o-*methoxyphenyl*-5-o-*hydroxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one*-2-*carboxylate* (VII) was obtained from the above alkaline filtrate after dilution with water and treatment with dilute acetic acid. After dissolution in carbon disulphide and removal of the supernatant liquid from tarry matter, a solid separated out which crystallised

from the same solvent in yellow prisms, m. p. 159—161°. The solution in dilute alkali is yellow, in concentrated sulphuric acid, deep red. The *dimethyl ether* was identical with the dimethoxy-*cyclo*hexenone obtained from 2 : 2′-dimethoxydistyryl ketone (Found: C = 73·3; H = 6·0. $C_{24}H_{24}O_5$ requires C = 73·5; H = 6·1%).

2-*Acetyl*-3-o-*methoxyphenyl*-5-o-*methoxystyryl*-$\Delta^5$-cyclo*hexen*-1-*one* (V).—A mixture of 2 : 2′-dimethoxydistyryl ketone (6 gms.; 1 mol.), acetylacetone (1¼ mols.), and 50 c.c. of hot alcohol was treated with sodium hydroxide solution (8 c.c. of 10%) and kept for 4 hours, when a small quantity of the *cyclo*hexenone separated out, and the remainder on dilution of the filtrate. Crystallised from alcohol and then from benzene–ligroin, it formed pale yellow prisms, m. p. 174° (Found: C = 76·7; H = 6·4. $C_{14}H_{24}O_4$ requires C = 76·6; H = 6·4%). On heating this compound for 2 hours on the water-bath with a mixture of methyl-alcoholic potash and potassium hypoiodite solution, 3-*o*-methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one separated out, yellow crystals from acetone, identical with the methyl ethers obtained from compounds III and VIII.

In conclusion we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (T. A. F.) which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, June 4th*, 1924.]

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## CCLXXI.—*Selective Solvent Action by the Constituents of Aqueous Alcohol. Part III. The Effect of some Water-soluble Semi-solutes.*

By ROBERT WRIGHT.

THE effect of alcohol-soluble semi-solutes on the partial vapour pressures of a mixture of alcohol and water is to lower the vapour pressure of the alcohol and slightly to raise that of the water (J., 1923, **123**, 2493). The present paper deals with the results obtained for a series of water-soluble semi-solutes in a similar mixed solvent.

The experimental method was the same as that already described. Air, saturated with the mixed vapours, was analysed by combustion, and the partial pressures of the alcohol and water were calculated from the quantities of the products. The temperature of the solutions was 20° and the solvent contained 10 mol. per cent. (22·1 wt. per cent.) of ethyl alcohol. The concentration of the

solute was in all cases 0·5 gram-equivalent of salt in 1000 grams of solvent. The results are shown in the following table:

| Solute. | None. | None. | KCl. | NaCl. | $NH_4Cl$. | KBr. | NaBr. |
|---|---|---|---|---|---|---|---|
| V. p. of alc. | 13·4 | 13·0 | 14·2 | 14·2 | 13·9 | 13·9 | 13·9 |
| | 13·0 | 13·1 | 14·3 | 14·2 | 13·7 | 13·9 | 14·0 |
| V. p. of water | 16·1 | 16·4 | 15·3 | 16·1 | 14·9 | 16·1 | 16·1 |
| | 16·3 | 16·7 | 15·8 | 16·6 | 16·1 | 16·7 | 16·1 |

| Solute. | $KNO_3$. | $NaNO_3$. | $K_2CO_3$. | $Na_2CO_3$. | $Na_2SO_4$. | $(NH_4)_2SO_4$. |
|---|---|---|---|---|---|---|
| V. p. of alc. | 13·7 | 13·7 | 14·8 | 14·7 | 15·0 | 14·5 |
| | 13·6 | 13·7 | 14·7 | 14·9 | 15·2 | 14·7 |
| V. p. of water | 16·8 | 15·4 | 16·3 | 16·4 | 16·4 | 15·8 |
| | 16·7 | 16·4 | 16·7 | 16·3 | 16·0 | 16·2 |

The partial vapour pressures obtained for water are erratic and unsatisfactory. This is due mainly to two causes: (*a*) the low molecular weight of water vapour, so that a small error in the weight of water obtained causes a large error in the calculated vapour pressure; (*b*) any error in the estimation of the alcohol will affect the partial vapour pressure obtained for the water, since the weight of water vapour is the difference of the weight of water in the absorption tubes and that produced by the combustion of the alcohol. It is therefore not thought advisable to lay much stress on the pressures obtained for the water, but to consider only those for alcohol. It should be pointed out that the same considerations render doubtful the effect of benzyl alcohol in lowering the vapour pressure of water under certain conditions (*loc. cit.*).

In all cases, the alcohol vapour pressures are raised by the presence of a water-soluble semi-solute; but the effect has not a constant value, although the equivalent concentration of solute is always the same. It would seem, however, that the effects of the sodium and potassium salts of the same acid are almost identical, whilst the elevation produced by the ammonium salt is slightly less. Of the acid radicals, sulphates and carbonates have the greatest effect and nitrates and bromides the least. It may be that each ion produces its own independent effect, but the data are not sufficient to state that such is the case.

As a general conclusion from the results obtained, it may be stated that a semi-solute dissolved in aqueous alcohol lowers the vapour pressure of the constituent in which it is soluble and raises the vapour pressure of the other constituent. It would thus seem that even in the mixed solvent the solute is held in solution by that constituent which is capable of dissolving it when acting alone.

GLASGOW UNIVERSITY. [*Received, July 22nd,* 1924.]

# CCLXXII.—*The Conditions of Reaction of Hydrogen with Sulphur. Part V. Photochemical Union.*

By Ronald George Wreyford Norrish and Eric Keightley Rideal.

In a recent series of investigations (J., 1923, **123**, 696, 1689, 3202) we have made a study of the various reactions between sulphur and hydrogen and sulphur and oxygen at temperatures ranging from 240° to 350°, both in the gaseous and on the surface phases. Four distinct dark reactions have been distinguished, and these, together with certain allotropic and physical changes of sulphur itself, have been shown to have temperature coefficients indicating critical increments of activation which are in all cases simple multiples of a constant quantity, *ca.* 12,700 cals. Throughout the work, the hypothesis that the critical increments observed measure the energy required to activate the sulphur molecule alone by breaking of one or more bonds proved a consistent and valuable guide and is in accord with all the facts summarised in Table VI of our last paper (*loc. cit.*). If the hypothesis which has been brought forward is accepted, it will be seen that the simple multiple $n$, connecting the critical increment and the constant, is equal to the number of electrons constituting the valency bonds broken in the activation of the molecule, and according to G. N. Lewis's view of activation ("Valence," p. 157. Chemical monograph series. New York, 1923), the constant quantity 12,700 cals. may thus be looked upon as the energy required to raise each bonding electron in the sulphur molecule to some higher quantum level, a level which must be equivalent to complete dissociation of the valency bond.

It is thus evident that we must consider the methods by which active sulphur molecules are produced from inactive ones. There are two possible mechanisms: they may be produced by some process of kinetic activation, as, for instance, by the momentum exchange caused by mutual collisions between unactivated sulphur molecules exceeding a certain minimum value—a process which has been shown to lead to a consistent view of chemical reactivity* and one which is operative in reactions 7—8 and possibly in 1—4 also; or they may be produced by the absorption of temperature radiation from the system in terms of quanta, as suggested by Trautz, Perrin, and McC. Lewis in their radiation theory of chemical

* For discussion, see Norrish, *Chemistry and Industry*, 1924, **43**, 327; Sutton, *Phil. Mag.*, 1914, [vi], **28**, 798; Todd and Owen, *ibid.*, 1919, **37**, 225; Lindemann, *Trans. Faraday Soc.*, 1922, **17**, 546.

action,* for though the radiation theory is now discredited as a complete theory of chemical reactivity there is no reason why the process of activation by radiation should not in some cases occur simultaneously with the more general process of kinetic activation.

It therefore became of importance to inquire how far activation of the sulphur molecule could be brought about by radiation, and, if so, whether the critical increments observed above in the processes of kinetic activation bore any simple relation to the quantum of activating radiation. This work forms the experimental section of this paper, and the results obtained are in complete accord with the predictions of the radiation theory.

The gaseous reaction between hydrogen and sulphur has been found to be catalysed by ultra-violet light furnished by the mercury vapour lamp, while the absorption spectrum of $S_2$ vapour has been shown by Graham (*Proc. Roy. Soc.*, 1910—1911, **84**, *A*, 311), and also by the present authors, to have an absorption band with its head at the point predicted by the radiation theory. Thus the magnitude of the quantum of the photoactive radiation has been shown to be equal to the critical increment of the gaseous hydrogen sulphide reaction and also to the heat of dissociation of the $S_2$ molecule.

It is therefore now possible to state that activation of sulphur molecules may occur both by collision and by radiation, and that in all cases the quantity of energy absorbed per molecule is a simple multiple of a constant quantity associated with each bonding electron involved in the process of activation. It thus appears that, when activation by collision occurs, the Newtonian laws of inelastic impact do not hold, but that the process of activation will rather be found to obey the laws of quantum dynamics, the same amount of energy being extracted from the colliding molecules, whatever the force of their impact, provided always that this force of impact exceeds a certain limiting magnitude.

## Experimental.

### (1) *The Ultra-violet Absorption Spectrum of Sulphur Vapour.*

A study of the absorption spectrum of sulphur vapour has been made by Graham (*loc. cit.*), who distinguishes two bands, both showing fine structure at low pressures, one in the extreme violet, and commencement of the ultra-violet, the other much deeper in the ultra-violet. The former of these two bands he attributes to

* Papers by W. C. McC. Lewis, J., 1914—1922. General discussion by Faraday Society on the Radiation Theory, *Trans. Faraday Soc.*, 1922, **17**, 546. Earlier papers by Trautz, *Z. Wiss. Photochem.*, 1906, **4**, 160; Krüger, *Z. Elektrochem.*, 1911, **17**, 543.

$S_8$ molecules, inasmuch as it is strongly in evidence at low temperatures and high pressures, while the latter is attributed to $S_2$ molecules, since it makes its appearance at high temperatures and low pressures when the vapour consists nearly completely of $S_2$.

The point of maximum absorption for the $S_8$ band was estimated at $\lambda = 4000$ Å.U. and that for the $S_2$ band at $\lambda = 2667$ Å.U. Assuming the latter to be a photoactive wave-length for the activation of $S_2$ and calculating the critical increment of activation, $q$, therefrom according to the formula $q = Nh\nu$, where $N$ = Avogadro number, $h$ = Planck's constant, $\nu$ = frequency corresponding to active wave-length, we obtain $q = 106{,}570$ cals., or 53,280 cals. per gram-atom of sulphur.

This figure is in very close agreement with the critical increment of activation of the gaseous reaction between hydrogen and sulphur, 51,400 cals., and also with the heat of dissociation of the $S_2$ molecule, 50,000 cals., and suggests at once that ultra-violet light of *ca.* $\lambda = 2667$ Å.U. should be photochemically active in the gaseous reaction between hydrogen and sulphur. As is shown in the latter portion of this paper, this prediction has been verified.

It seemed of importance, however, to repeat Graham's work so far as it applies to the present work, and a study of the ultra-violet absorption spectrum of sulphur vapour was therefore undertaken with a view to obtaining with greater accuracy the point of maximum absorption. This has been carried out by a method differing somewhat in principle from that used by Graham.

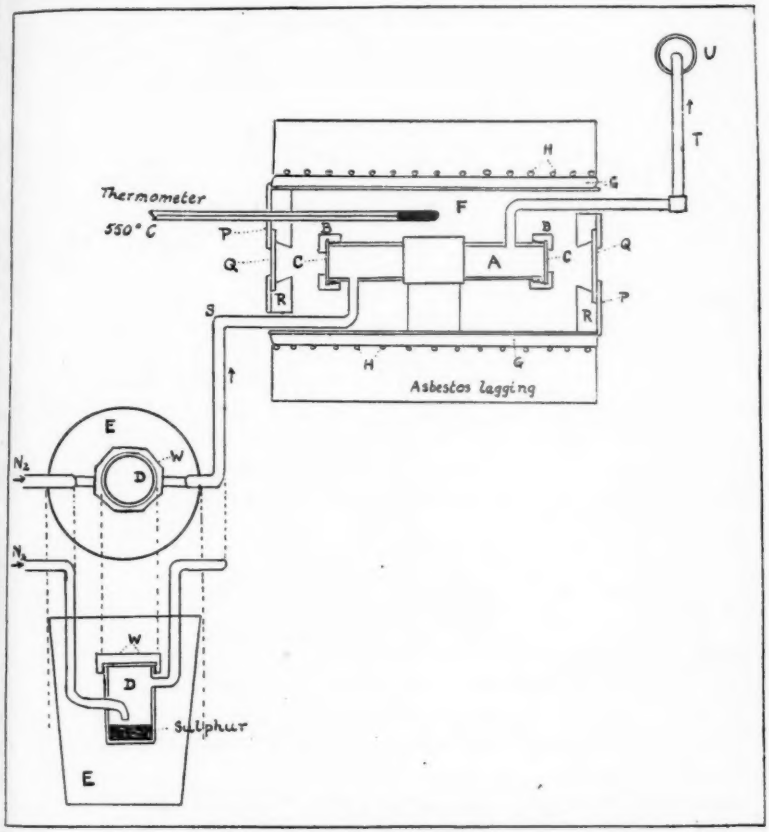
The apparatus used is shown in Fig. 1. The absorption tube, A, 3 inches long, $\frac{1}{2}$ inch in internal diameter, was closed at each end by quartz windows, C, C, kept in position by rings of asbestos paper, and screw nuts, B, B. The whole absorption tube was enclosed in an outer brass case, F, which could be regulated to any temperature up to 600° by means of the electrically heated nichrome wire, H, wound on a layer of asbestos, G, and lagged by four layers of tightly wound asbestos rope. The end of the brass case, F, was closed by two brass end pieces, P P, fitted with quartz windows, Q Q, kept in position by thick asbestos rings, R R.

A stream of pure nitrogen, charged with sulphur vapour at any desired pressure by passage through the sulphurettor D, was passed slowly through the absorption tube by way of the lagged iron inlet tube, S, and the iron outlet tube, T, after which it bubbled into the air through water contained in a test tube, U.

The sulphurettor, D, consisting of an iron vessel fitted with a screw cap, W, was kept at any desired temperature by regulating the temperature of the bath E, consisting of the eutectic mixture of sodium and potassium nitrates.

The source of light used was an iron arc, and photographs of the absorption spectrum of sulphur vapour were obtained for various pressures and temperatures of the sulphur vapour by photographing the arc through the absorption tube, using a quartz spectrograph. As a result of numerous observations, the position and fine structure of the band obtained by Graham for $S_2$ vapour have been confirmed

FIG. 1.




*Light absorption tube for $S_2$ vapour at varying pressures.*

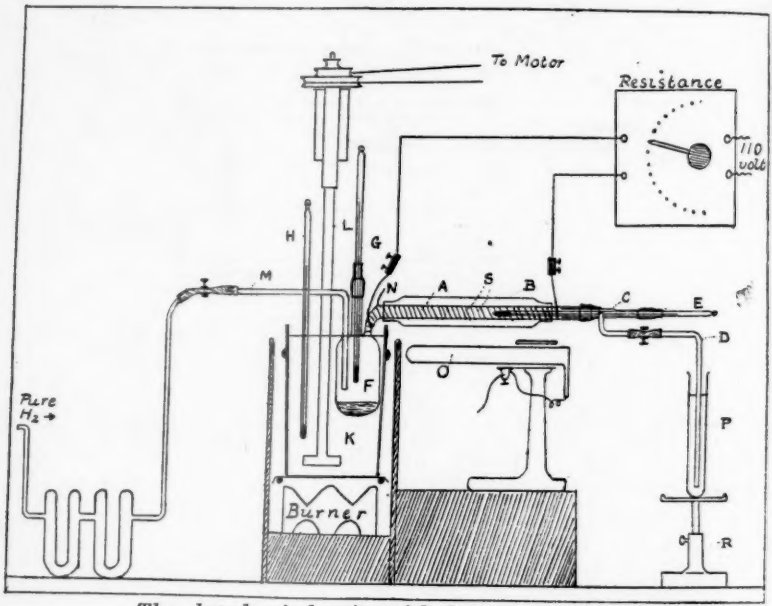
and from a careful comparison of the photographs we consider that the point of maximum absorption is at $\lambda = 2750$ Å.U. This gives a value of $q = Nh\nu = 103{,}350$ cals., or 51,670 cals. per gram-atom of sulphur, an absolute agreement with the data summarised in Table VI of our last paper (*loc. cit.*). Photographs of the mercury vapour spectrum taken through the sulphur vapour indicated that some eight lines between $\lambda = 2970$ and $\lambda = 2570$ inclusive were

selectively absorbed, the lines most strongly absorbed being those at $\lambda = 2805$, 2759, and 2700. These lines lie closely round the head of the absorption band and therefore may be considered the photochemically active wave-lengths of the mercury vapour spectrum.

(2) *The Photochemical Combination of Hydrogen and Sulphur.*

The apparatus shown in Fig. 2 was designed to enable a mixture of hydrogen with sulphur vapour at varying partial pressures to

FIG. 2.




*The photochemical union of hydrogen and sulphur.*

be exposed at various temperatures to the light of a mercury vapour lamp.

A stream of dry hydrogen, carefully purified from oxygen, was passed into the sulphur bulb, F, by way of the inlet tube, M. After becoming charged with sulphur vapour, it passed out at N, and into the tube A, heated electrically to the desired temperature by means of the nichrome wire S. The gas stream, after slowly passing through the tube A, was allowed to bubble slowly by way of the adapter, C, through *N*/10-caustic soda solution contained in the test-tube P. Any hydrogen sulphide in the gas stream was absorbed by the soda and could be estimated colorimetrically (*loc. cit.*, p. 698). The hot tube A and the sulphur bulb F were made of

clear quartz, all in one piece. An outer tube of clear quartz, B surrounded the nichrome wire winding of A, and served to protect the inner tube from variations of temperature due to air currents. The temperature of the gas stream in A was measued by the thermometer E. The sulphur bulb was kept heated at the desired temperature by means of a salt bath consisting of the eutectic mixture of sodium and potassium nitrates, kept well stirred and regulated by hand to $\pm 0{\cdot}25°$.

The hot tube A was always maintained at a considerably higher temperature than the sulphur bulb, so that no condensation of sulphur occurred on the walls, and thus the mixed hydrogen and sulphur gases could be exposed directly to the light of the double-barrelled mercury vapour lamp O, supported immediately below the hot tube. The following measurements were then carried out. With the sulphur bulb at 245°, hydrogen was passed through the apparatus at a constant velocity, and the quantity of hydrogen sulphide formed per second estimated

(1) with the lamp off,
(2) with the lamp on, but with the tubes A and B shielded from ultra-violet radiation by a thick glass sheath,
(3) with the lamp on and the tubes A and B unshielded,

measurements being made with the exposed tube kept at 300°, 310°, 320°, 330°, and 340° respectively.

In the first case the vapour was thus unexposed to the lamp, in the second it was exposed to the visible radiations only, while in the third case it was exposed both to the visible and the ultra-violet radiation. Throughout a given experiment the temperature of the hot tube was kept constant to $\frac{1}{2}°$ by regulating the heating current with a variable resistance.

The results of the series of experiments are shown in Table I, columns 2, 3 and 4.

The close agreement of the figures in columns 2 and 3 indicates that the visible radiation of the mercury vapour lamp produces no acceleration of the dark reaction, while the results in column 4 show that the admission of ultra-violet radiation to the system more than doubles the reaction velocity. By subtracting the figures for the dark reaction in column 2 from the corresponding figures of column 4, we obtain column 5—the increment of reaction velocity due to the light—which may be termed the *photochemical reaction*.

On plotting the logarithms of the dark reaction and of the photochemical reaction velocities against the reciprocal of the absolute temperature (Fig. 3), we obtain two approximately straight lines,

## TABLE I.

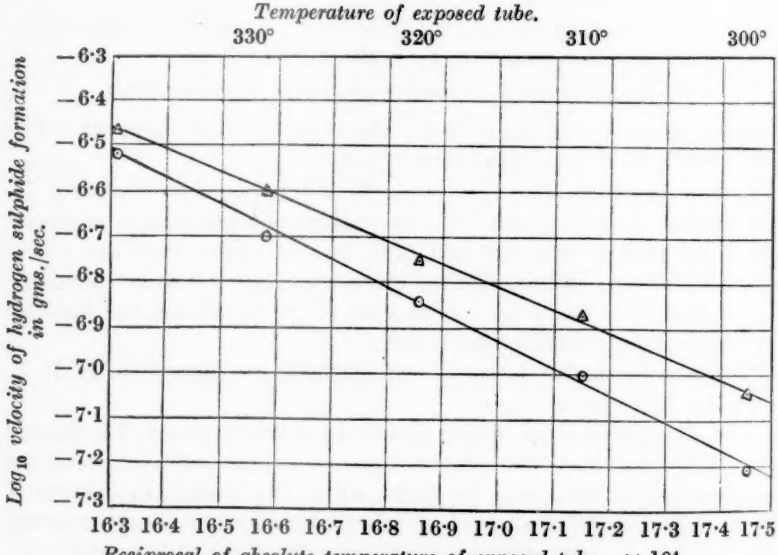
### *Effect of Temperature.*

Temperature of sulphur bulb 245°. Pressure of sulphur vapour 6·3 mm. of Hg. Rate of flow of gas 200 c.c. per hour. Refer to Fig. 3.

Velocity of $H_2S$ formation in gms. per sec. $\times 10^8$.

| Temp. of exposed tube. | Tube dark. | Tube illuminated, ultra-violet excluded. | Tube illuminated, ultra-violet admitted. Two determs. at each temp. | Mean. | Photochemical reaction. |
|---|---|---|---|---|---|
| 300° | 6·15 | 6·75 | 15·87<br>14·48 | 15·14 | 8·99 |
| 310 | 10·26 | 10·95 | 22·32<br>24·95 | 23·63 | 13·37 |
| 320 | 14·20 | 15·20 | 33·09<br>30·21 | 31·65 | 17·45 |
| 330 | 20·04 | 21·90 | 45·88<br>43·86 | 44·87 | 24·83 |
| 340 | 31·07 | 34·04 | 65·75<br>65·16 | 65·46 | 34·39 |

FIG. 3.




⊙ *Dark reaction.* $\eta = 1{\cdot}48$. △ *Photochemical reaction.* $\eta = 1{\cdot}38$.
*Temperature of sulphur bulb in all cases* 245°.

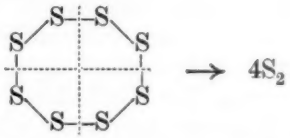
from the slopes of which the temperature coefficients of the reactions may be obtained. These are found to be

| | |
|---|---|
| Dark reaction ... ... ... ... ... ... | 1·48 |
| Photochemical reaction ... ... ... ... | 1·38 |

The temperature coefficient of the dark reaction is constant and equal to that previously found for the surface reaction between hydrogen and sulphur and indicates, therefore, the absence of any observable gaseous reaction. Under the same conditions the temperature coefficient of the photochemical reaction is constant and considerably greater than that found for most photochemical reactions.

To account for this we may suppose that the photochemically active species, $S_2$, is removed by the light to give hydrogen sulphide as fast as it is formed, with the result that the back reaction of the equilibrium $S_8 \rightleftharpoons 4S_2$ is very largely suppressed.

The photochemical reaction velocity will then be limited by the rate at which the $S_8$ molecules break up, a rate which will be dependent on the temperature of the hot tube. If the $S_2$ molecules are produced, as is most probable, by the splitting of $S_8$ rings according to the scheme



the temperature coefficient, according to the theory which has been found to hold good throughout this work, should be 1·48. That the value found is somewhat less than this, may be reasonably attributed to the fact that the back reaction of the equilibrium referred to above is not completely suspended, but still takes place to a small extent.

TABLE II.

*Effect of Pressure of Sulphur Vapour.*

Temperature of exposed tube 320°. Rate of flow of gas 200 c.c. per hour.

| Temp. of sulphur bulb. | Partial pressure of sulphur vapour (mm. Hg). | Velocity of $H_2S$ formation in gms. per sec. × $10^8$. Dark reaction; ultra-violet excluded. | Total reaction; ultra-violet admitted. | Photo-chemical action. | Dark reaction velocity divided by sulphur pressure. | Photo-chemical reaction velocity divided by sulphur pressure. |
|---|---|---|---|---|---|---|
| 235° | 5·25 | 13·7 | 25·3 | 11·6 | 2·62 | 2·22 |
| 245 | 6·30 | 15·2 | 31·6 | 16·4 | 2·41 | 2·60 |
| 255 | 7·60 | 17·7 | 35·1 | 17·4 | 2·33 | 2·29 |
| 265 | 9·10 | 20·2 | 40·9 | 20·7 | 2·22 | 2·27 |

In Table II is shown the result of keeping the temperature of the exposed tube constant at 320°, and varying that of the sulphur bulb between 235° and 265°. By this means the effect of variation of the partial pressure of the sulphur vapour is observed, since,

for the slow rate of gas flow used, the sulphur vapour will be taken up by the hydrogen to the extent of its vapour pressure at the temperature of the sulphur bulb. From the approximate constancy of the figures in column 6, the dark reaction velocity is seen to be proportional to the partial pressure of the sulphur vapour, and, since this reaction has been shown above to be a surface reaction, it follows that the concentration of the layer of sulphur adsorbed on the quartz surface of the exposed tube increases proportionately with the pressure of sulphur vapour. At the same time the concentration of the photochemically active $S_2$ molecules in the gaseous phase also increases with pressure, resulting in an increase in velocity of the photochemical reaction * proportionate to the increase of the partial pressure of sulphur, as is seen from column 7.

The effect of increasing the quartz surface was investigated by supporting a second quartz tube, closed at both ends, coaxially inside the exposed tube. This increase of surface produced a proportionate increase in the dark reaction velocity while it left the photochemical reaction somewhat diminished, as shown in Table III, thus confirming the conclusions, already arrived at, that the former takes place on the surface while the latter occurs in the gaseous phase.

## TABLE III.

### *Effect of Surface.*

Temperature of sulphur bulb 245°. Pressure of sulphur vapour 6·3 mm. of Hg. Temperature of exposed tube 320°. Rate of flow of gas 200 c.c. per hour.

| Lamp. | Surface extent: sq. cms. | Rate of $H_2S$ formation in gms. per sec. × $10^8$. Total reaction. | Photochemical reaction. | Vel. of dark react. / Total surface. |
|---|---|---|---|---|
| Off | 84·7 | 18·1 | 0 | 0·214 |
| Off | 84·7 | 18·3 | 0 | 0·216 |
| Off | 67·4 | 14·2 | 0 | 0·211 |
| On | 84·7 | 30·4 | 12·2 | |
| On | 84·7 | 29·5 | 11·3 | |
| On | 67·4 | 31·6 | 17·4 | |

The diminution in the photochemical reaction is seen by comparing the figures in column 4, which are calculated by subtracting the total dark from the total light reactions of column 3, and is to be accounted for by the large diminution in volume of the exposed tube consequent upon inserting the inner closed quartz tube.

* Calculated as before.

*Sources of Error in the Experimental Determinations.*

The trustworthiness of the methods adopted in the present paper for comparing reaction velocities has already been proved in the previous papers of this series, and the figures for the dark reaction, when precautions are taken to purify the hydrogen completely from traces of oxygen, are accurate to 1 per cent. There is, however, in the case of the illuminated reaction, a minor source of error in the fluctuations of the lamp, but it will be seen from the concordance of the duplicate "runs" in column 4 (Table I) that these variations are not serious and do not amount to more than 6 per cent. Finally, blank experiments were carried out, keeping the exposed tube at atmospheric temperature, to see if any appreciable quantity of hydrogen sulphide was formed in the sulphur bulb. Thus with the sulphur bulb at 245°, the rate of formation of hydrogen sulphide was $0{\cdot}15 \times 10^{-8}$ gm. per second, a quantity which would introduce an error of less than 1 per cent. in the determinations recorded above.

*The Photochemically Active Radiation.*

From the fact that the visible radiations of the mercury lamp have been demonstrated above to be non-active towards sulphur, it follows that the photochemically active rays of the mercury vapour spectrum for the reaction under consideration are the three lines $\lambda = 2805$, $\lambda = 2759$, and $\lambda = 2700$, the only other radiation strongly absorbed by the sulphur vapour.

The critical increments of activation per gram-atom of sulphur corresponding to these wave-lengths are 50,650 cals., 51,500 cals. and 52,600 cals., numbers in very close agreement with the value of 51,460 cals. calculated from the temperature coefficient of the gaseous $H_2S$ reaction, and the value of 50,000 cals., the heat of dissociation of the $S_2$ molecule. The predictions of the radiation theory are in this case thus fully confirmed.

*General Conclusions.*

The present paper forms the last of a series dealing with the reactivity of mixtures of sulphur with hydrogen and oxygen and it may be well briefly to indicate the general conclusions which have been arrived at concerning the problem of chemical reactivity as a result of this work. It is well known from the work of Preuner and Schupp (*Z. Physikal. Chem.*, 1909, **68**, 129) that the molecules of sulphur vapour can exist in at least two forms, $S_8$ and $S_2$, and possibly also as $S_4$.

In addition, liquid sulphur consists of a mixture of two forms of

sulphur, $S_\mu$ and $S_\lambda$, of which one form is of composition $S_8$. This must be the chief component of the surface layer of liquid sulphur, at temperatures round 300°, since this surface is in equilibrium with a vapour largely composed of $S_8$ molecules. Reactions between hydrogen and sulphur and oxygen and sulphur can take place only between sulphur *atoms* in the gaseous phase, which are produced both as a result of collision and also as a result of photochemical dissociation. The dark reaction is thus accelerated by ultra-violet light of the requisite frequency.

Reaction at the surface takes place between activated $S_8$ molecules already present in the system and hydrogen. Oxygen, inasmuch as it can poison this $H_2S$ surface reaction with the concomitant formation of sulphur dioxide, can also react with these active molecules. It can, however, as in the case of the A and B surface reactions, also react with unactivated sulphur molecules, inaccessible to the hydrogen, to an extent proportional to its pressure. It is assumed that the oxygen molecule can activate these sulphur molecules by collision, a feat impossible to the hydrogen molecule at the same temperature by reason of its much smaller average momentum (J., 1923, **123**, 3202). In all cases where reactions can be traced between sulphur and sulphur, sulphur and hydrogen, and sulphur and oxygen, the critical increment is a multiple of a constant quantity. This multiple is probably equal to the number of bonding electrons involved. Activation of the sulphur molecule, whether $S_2$ or $S_8$, as far as the reactions considered in the present series are concerned is thus regarded as synonymous with the dissociation of a valency " bond." This activation may take place both by radiation and by collision, and in the latter case both in the gaseous phase and at a surface, and in all cases the energy of activation remains the same. There seems to be no way of accounting for this remarkable fact upon a basis of Newtonian mechanics, and it appears that kinetic activation must also be subject to the laws of quantum dynamics.

It will thus be seen that the concept of chemical activation arrived at as a result of the study of the reactivity of the sulphur molecule has much in common and is probably identical with the physicist's view of processes included under the term molecular excitation. It is highly desirable that this point should be either confirmed or disproved, not only because of the frequent misuse of the term activation, *e.g.*, in activated charcoal, but also to avoid those difficulties always associated with alternative terminology for identical concepts.

*Summary.*

(1) The data of previous work on the reactions of sulphur, with reference to current theories of chemical reactivity, are discussed.

(2) Evidence is furnished suggesting that molecular activation, whether kinetic or by radiation, is a quantum phenomenon.

(3) The work of Graham on the absorption spectrum of $S_2$ vapour has been partly repeated and confirmed, except that the point of maximum absorption is located very slightly more towards the red end of the spectrum, at $\lambda = 2750$ Å.U.

(4) This wave-length corresponds on the radiation theory with a critical increment of 51,670 cals. per gm.-atom of sulphur, a number in exact agreement with that calculated from the temperature coefficient of the "thermal" gaseous reaction between hydrogen and sulphur.

(5) Ultra-violet radiation of this wave-length, in agreement with hypothesis, was found to be active in initiating a photochemical reaction between hydrogen and sulphur vapour, proportional to the pressure of the sulphur vapour.

(6) General conclusions arrived at respecting chemical reactivity are indicated. Activation or excitation of the sulphur molecule is regarded as synonymous with the dissociation of one or more bonds, and may take place either by collision or by radiation. The quantity of energy absorbed per atom is independent of the mechanism of activation, and is a function only of the number of bonds destroyed per atom.

Department of Physical Chemistry,
Cambridge University. [*Received, May 7th*, 1924.]

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## CCLXXIII.—*Studies of Dynamic Isomerism. Part XVI. The Mutarotation of Beryllium Benzoylcamphor. Formation of an Additive Compound with Chloroform. The Optical Activity of Beryllium.*

By Henry Burgess and Thomas Martin Lowry.

### 1. *Prototropy and Co-ordination.*

In a recent paper on "The Polarity of Double Bonds" (Lowry, J., 1923, **123**, 822; compare Lowry and Burgess, *ibid.*, 2111), it was suggested that a very close connexion should exist between *prototropy*, *i.e.*, the special form of dynamic isomerism which depends on the migration of a proton or mobile hydrogen atom, and *co-ordination* of the cyclic type. Both phenomena can, in fact.

be traced back to the existence of a multipolar anion. Such an ion, by attracting a proton to one or other of its negatively-charged poles, can give rise to a series of isodynamic hydrides; whilst, if a proton or a metallic kation is attracted simultaneously to two of the negative poles, a co-ordination compound of the cyclic type will be produced. The best substance for investigating this question experimentally appeared to be benzoylcamphor, of which we had a supply prepared in readiness for further studies of its dynamic isomerism. Several of its metallic derivatives were therefore prepared and examined with a view to find out how far they possessed the typical properties of co-ordination compounds; and special attention was directed to the colourless compounds, on the ground that full advantage could be taken of their optical activity. It was in the pursuit of this policy that we were led to the discovery of the fact that the beryllium compound exhibits the property of mutarotation. In the great majority of cases that have been studied hitherto, this phenomenon has depended on the existence of a mobile hydrogen atom, and has been arrested by methylation or by the formation of metallic derivatives; the fact that mutarotation occurs, not only in benzoylcamphor itself, but also in a derivative in which all the mobile hydrogen has been replaced by a metal, opens out a new chapter in the study of mutarotation. In this respect, the new observation can indeed be compared with the discovery, made 25 years ago (J., 1899, **75**, 211), that nitrocamphor undergoes mutarotation in anhydrous solvents, thus proving that this phenomenon can be produced as a result of reversible isomeric change, as well as by the reversible hydration of compounds such as gluconolactone.

### 2. *Mutarotation and Solubility.*

Beryllium benzoylcamphor is a stable compound, which forms colourless, tabular crystals, and has no tendency to decompose on keeping. It has a very high rotatory power, and the mutarotation in benzene, although slow, is quite substantial, since the specific rotation decreases to the extent of nearly 50° in the course of a week or ten days. In view of the novelty of the observations, however, it was thought that the change producing the mutarotation was perhaps not reversible, and might be merely a commonplace decomposition of the substance to a camphor compound of lower rotatory power. This supposition was disproved by allowing a solution in benzene, of which the rotatory power had reached a steady value, to evaporate slowly to dryness; the solid was then dissolved in the same volume of benzene, when the rotatory power of the compound was found to have returned to its former high

value, showing that the change which causes the mutarotation had been reversed completely during the slow crystallisation of the solution. Changes of rotatory power were also observed in freshly prepared solutions in chloroform, acetone, heptane and *cyclo*hexane, as set out in Table I, thus proving that the phenomenon is definitely characteristic of the solute, and does not depend on the selection of a particular type of solvent. Moreover, the change of rotatory power does not result in any change in the molecular weight of the solute, as measured by the freezing point of its solutions in benzene.

TABLE I.

*Rotatory Power of Beryllium Benzoylcamphor at* 20°.

| Solvent and Concentration. | | $[\alpha]_{5461}$ Initial. | $[\alpha]_{5461}$ Final. | $[M]_{5461}$ Initial. | $[M]_{5461}$ Final. | Velocity constant. |
|---|---|---|---|---|---|---|
| (*a*) Benzene | 8 g./100 c.c. | 490° | §458° | 2547° | §2380° | 0·0055 per hr. |
| (*b*) ,, | 9·45 g./100 c.c. | ‡487 | §448 | 2532 | §2334 | 0·044 ,, ,, |
| (*c*) ,, | 5%+0·094% $C_5H_{11}N$. | ‡489 | 443 | 2540 | 2300 | 0·0060 ,, min. |
| (*d*) ,, | 5%+0·18% $C_5H_{11}N$. | ‡486 | 444 | 2526 | 2306 | 0·0167 ,, ,, |
| * ,, | 3·426%+1·575% $CHCl_3$ | †443 | 443 | †2300 | 2300 | |
| (*e*) Chloroform | 9·663 g./100 c.c. | ‡450 | 385 | 2340 | 2000 | 0·0231 ,, ,, |
| (*f*)* ,, | 10·29%+4·72% $CHCl_3$. | †395 | 385 | — | 2000 | 0·0227 ,, ,, |
| (*g*) Acetone | 1·64 g/100 c.c. | †425 | 383 | †2210 | 1990 | 0·056 ,, ,, |
| (*h*) Alcohol | 0·3g./100 c.c. | | 374 | | 1940 | |
| (*i*) ‖Heptane | 0·195 g./100 c.c. | ‡446 | — | ‡2315 | — | 0·018 ,, ,, |
| | 0·438 g./100 c.c. | — | 374 | — | 1940 | |
| (*j*) ‖*cyclo*Hexane | 0·460 g./100 c.c. | ‡450 | — | ‡2340 | — | 0·0023 ,, ,, |
| | 1·240 g./100 c.c. | — | 372 | — | 1930 | |

* Chloroform-compound taken, but treated as a mixture of the parent-compound with the addition of the calculated percentage of chloroform.

† Initial value reduced by mutarotation.

‡ Initial value calculated back to zero time.

§ Final value probably high on account of evaporation.

‖ Saturated solutions.

It was therefore clear that the mutarotation of beryllium benzoylcamphor, like that of nitrocamphor, is due to reversible isomeric change and provides another example of the phenomenon of dynamic isomerism.

The rotatory powers shown in the above table are of interest on account of the relative uniformity of the rotatory powers in all solvents *except benzene*, which gives specific rotations some 50° higher than the others, recalling the precisely similar behaviour of nitrocamphor in aromatic solvents (J., 1899, **75**, 217). The initial values were obtained by extrapolating to zero time, and are therefore less accurate than the final values, except in the case of benzene, where the mutarotation was extremely slow.

The speed of the mutarotation is increased very greatly by the action of catalysts such as piperidine and benzoic acid (compare J., 1903, **83**, 1314; 1908, **93**, 107); the latter compound, however, also brings about a non-reversible decomposition, giving rise probably to the production of beryllium benzoate. The mutarotation was also found to be normal in that it was accompanied by a progressive increase of solubility (compare J., 1904, **85**, 1541, 1551). By measuring the solubility of beryllium benzoylcamphor in heptane and in *cyclo*hexane, before and after adding a trace of piperidine, it was found that the proportion of the original compound in the final equilibrium is approximately one-half, just as in the case of α-glucose in methyl alcohol. Observations of the rotatory power of the saturated solutions also made it possible to predict the rotatory power of the labile isomeride (or mixture of labile isomerides) in heptane as $[\alpha]_{5461} = 292°$, $[\alpha]_{5780} = 246°$, approximately. Since we suppose that the two forms of the compound differ only in the sign of the rotation of an optically active beryllium atom, it appears that the partial specific rotation of the beryllium complex in these compounds is about $(448° - 292°) \div 2 = 78°$, whilst its molecular rotatory power must be of the order of 400° for $Hg_{5461}$.

3. *Formation of an Additive Compound with Chloroform.*

When beryllium benzoylcamphor is crystallised from a mixture of chloroform and acetone, it separates in tough, glassy prisms instead of the usual round, tabular crystals. These prisms contain two molecular proportions of chloroform, which is gradually lost on keeping the crystals, with the result that the surface of the prisms becomes opaque. The formation of this additive compound recalls the observations of Norris (*J. Amer. Chem. Soc.*, 1916, **38**, 702; 1920, **42**, 2086) on the addition of 2 mols. of chloroform to tetraphenylethylene dichloride, and of Jacobs and Heidelberger (*J. Biol. Chem.*, 1915, **21**, 105, etc.) on the addition of chloroform to the salts of hexamethylenetetramine.

If heated slowly from ordinary temperatures, the chloroform-compound does not melt until 204°, but if plunged into a bath at 80° it melts at once to a cloudy liquid, which solidifies again and remelts at the higher temperature. When the prisms are dissolved in acetone or benzene, the initial rotatory power of the solution (after about 15 minutes only) is identical with the final rotatory power, as reached after about a week in solutions of the tabular crystals of beryllium benzoylcamphor. When the prisms were dissolved in chloroform, the last stages of a rapid mutarotation were observed.

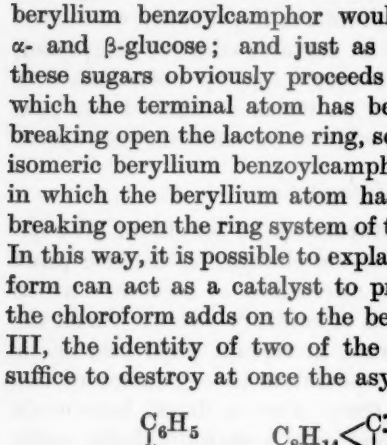
These observations suggest that chloroform acts as a catalyst in promoting the chemical change that gives rise to mutarotation. This conclusion was confirmed by dissolving the tabular crystals of beryllium benzoylcamphor in chloroform, when a condition of equilibrium was reached in 6 hours as compared with about a week in benzene. This result is directly contrary to the behaviour of chloroform when used as a solvent for nitrocamphor, since it was in this solvent that the arrest of mutarotation was first observed (J., 1899, **75**, 211), although nearly ten years elapsed before the origin of this arrest was discovered in the anti-catalytic action of carbonyl chloride (J., 1908, **93**, 119) formed by oxidation of the chloroform and present as an impurity in it. In the present instance, the catalytic action of chloroform is probably associated very closely with its ability to form an unstable additive compound, since (apart from "action at a distance," *e.g.*, by radiation) it is difficult to think of any other way in which a catalyst can act, except by adding on to and splitting off from the substance catalysed.

### 4. *Origin of the Mutarotation.*

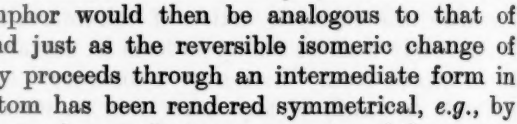
Apart from the fact that the mutarotation of beryllium benzoylcamphor is due to a reversible isomeric change, no definite proof can be given of the nature of the alterations of structure which bring about the observed alterations of rotatory power. Since the ketonic form of benzoylcamphor can, in theory, yield two enolic isomerides, it would be possible to postulate the existence of two enolic beryllium salts, or even of three, since a diacid base could obviously give rise also to a mixed salt containing both enolic radicals. Since, however, the beryllium derivative is obviously co-ordinated, we are reluctant to accept the view that two isomeric unco-ordinated forms are present as the main constituents of a solution of this compound in benzene. This assumption is, moreover, not necessary, since there are sound experimental reasons for recognising the existence of two isomeric co-ordinated forms of the compound.

This view is based upon the fact, which Morgan and Bragg (*Proc. Roy. Soc.*, 1923, **104**, 437) have established by the *X*-ray analysis of basic beryllium acetate, that *each beryllium atom in the co-ordinated complex is surrounded by four oxygen atoms situated at the corners of a tetrahedron of which the beryllium atom occupies the centre.* On assigning a similar configuration to beryllium benzoylcamphor, it is seen at once that, since the benzoylcamphor radical is unsymmetrical, *two* stereoisomeric forms of the co-ordination compound (I) are possible. In both these forms, moreover, the beryllium atom would be asymmetric, in just the same way as the central

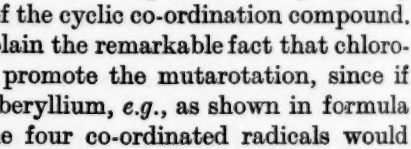
carbon atom of the diketolactone of benzophenonetetracarboxylic acid (II), recently prepared in optically active forms by Mills and Nodder (J., 1920, **117**, 1407). In view of the tetrahedral configuration of the beryllium complex, *cis*- and *trans*-isomerism is not possible, and two stereoisomerides can only be formulated in consequence of the fact that the asymmetric beryllium atom may be represented as either dextro or lævo in sign. This isomerism is in fact closely analogous to that of the α- and β-methylglucosides, where the terminal carbon atom becomes optically active on passing from the aldehydic to the lactonic form of the sugar, and thus gives rise to two series of stereoisomeric glucosides, differing only in the sign of the terminal carbon atom. The dynamic isomerism of beryllium benzoylcamphor would then be analogous to that of α- and β-glucose; and just as the reversible isomeric change of these sugars obviously proceeds through an intermediate form in which the terminal atom has been rendered symmetrical, *e.g.*, by breaking open the lactone ring, so the interconversion of the stereoisomeric beryllium benzoylcamphors must proceed through a form in which the beryllium atom has lost its optical activity, *e.g.*, by breaking open the ring system of the cyclic co-ordination compound. In this way, it is possible to explain the remarkable fact that chloroform can act as a catalyst to promote the mutarotation, since if the chloroform adds on to the beryllium, *e.g.*, as shown in formula III, the identity of two of the four co-ordinated radicals would suffice to destroy at once the asymmetry of the central atom.



(I.)



(III.)



(II.)

This view of the origin of the mutarotation is, it must be confessed, entirely speculative in character; but we have not been able to discover any equally plausible alternative explanation, and are satisfied that no other view is likely to bring the observations into such close relationship with the facts. In particular, it is clear that the mutarotation of beryllium benzoylcamphor is fundamentally different from that of the parent compound, which changes only with extreme slowness when dissolved in chloroform; it is therefore impossible to regard it as depending on a chemical change of the same type as the familiar prototropic changes which have

been studied hitherto. The correctness of our explanation would be conclusively vindicated if it should prove to be the case that a mutarotation catalysed by chloroform is possible in optically active co-ordination compounds, with a co-ordination number of 4 or 6, but impossible in the case of co-ordinated hydrogen, or of univalent metals, with a co-ordination number of 2.

The question of the optical activity of beryllium, which arises from these observations, is being followed up in this laboratory, and we desire to reserve this field of work for further investigation.

## Experimental.

5. *Preparation and Properties of Beryllium Benzoylcamphor.*—Piperidine (20 c.c.) was added to benzoylcamphor (50 gms.) dissolved in hot aqueous alcohol (150 c.c.). The precipitate formed on adding hydrated beryllium sulphate (18 gms., dissolved in the least quantity of water), was filtered off, after heating on the water-bath for 1 hour and allowing to cool, and was then washed with water; a further small quantity of the compound was obtained on evaporating off the alcohol. Total yield 97 per cent. The pale pink precipitate was recrystallised, from acetone containing small quantities of benzene or chloroform, until colourless; after two further crystallisations, it melted sharply at 208° (Found: C = 78·63; H = 7·57; Be = 1·76. $C_{34}H_{38}O_2Be$ requires C = 78·56; H = 7·38; Be = 1·75 per cent.).

Beryllium benzoylcamphor is insoluble in water, slightly soluble in the alcohols, more soluble in acetone, and very soluble in benzene or chloroform. From acetone it crystallises in circular, transparent plates (or in rosettes of these plates) which melt to a pale green liquid. On one occasion, however, four crystals of a tetragonal form separated (see below, § 7). These had the same melting point, 207°, as the plates which crystallised at the same time, and caused no depression of the melting point of these plates. They also possessed the same rotatory power $[\alpha]_{5461} = 480°$, $[\alpha]_{5780} = 400°$ in benzene (0·33 gm. per 100 c.c.) as that of the plates, $[\alpha]_{5461} = 485°$, $[\alpha]_{5780} = 402°$ in benzene (0·28 gm. per 100 c.c.); and their densities and refractive indices agreed within the limits of experimental error. Further attempts to grow similar crystals were unsuccessful, since, even when the solution was seeded with small portions of one of the crushed crystals, the usual tabular crystals were developed from these nuclei.

6. *Preparation and Properties of the Chloroform Compound.*—The chloroform compound, $(C_{17}H_{19}O_2)_2Be,2CHCl_3$, separates in long, transparent, four-sided prisms from a solution containing approximately equal parts of acetone and chloroform (Found: Cl = 27·84;

$CHCl_3 = 30{\cdot}85$. $C_{34}H_{38}O_2Be,2CHCl_3$ requires Cl = 28·05; $CHCl_3$ = 31·49 per cent.). It gradually loses chloroform, the transparent prisms becoming covered with an opaque layer. When covered with acetone, the crystals break up into a fine powder, the particles of which serve as nuclei for the separation of beryllium benzoyl-camphor in the ordinary form. The molecular rotatory powers of the additive compound, when in a condition of equilibrium in benzene, acetone, or chloroform, were identical with that of the parent substance, after allowing for the presence of 2 mols. of chloroform of crystallisation.

7. *Crystallographic Properties.*—The following data were obtained by Mr. R. Jeffery of Peterhouse, under the direction of Mr. A. Hutchinson, F.R.S.

(a) *Circular Plates.* These curious forms showed no crystal outline except the basal plane, which in most cases was perfectly flat. Towards the edges irregularities were frequent, but even there no twinning was detected. The whole crystal extinguished simultaneously between crossed Nicols, and with convergent light a uniaxial chromatic figure was obtained, which was negative in sign. This figure gave no indication of circular polarisation, but possibly the plate was not thick enough to show the effect. The *refractive indices*, determined by total reflection in Thoulet's solution, were $\omega = 1{\cdot}661$, $\epsilon = 1{\cdot}616$. The *specific gravity*, determined by flotation in Thoulet's solution, was 1·176.

(b) *Tetragonal Crystal* (Fig. 1). This crystal had the following properties:

*System*: Tetragonal.

*Axial Ratios*: $a : b : c = 1 : 1 : 1{\cdot}7324$.

*Habit*: The crystal was of tabular habit, the faces of the same form varying considerably in size. The predominant face is *z*(031), but in the zone where its faces are smaller *e*(011) is also present. The crystal was not well suited for measurement, since in some cases the images obtained from one face were spread over 2°. Measurement was also complicated by parallel growths.

*Forms present*: *C*(001), *e*(011), *z*(031); reflections corresponding to *t*(332) were also obtained on one corner.

| Angles observed. | No. of measurements. | Limits. | Mean observation. | Calculation. |
|---|---|---|---|---|
| *Ce* 001 : 011 | 3 | 59° 54′—60° 4½′ | 60° 0½ | — |
| *Cz* 001 : 031 | 8 | 79 15½—79 48½ | 79 51 | 79° 6½′ |
| *zz′* 031 : 301 | 8 | 88 49 —87 42 | 88 22 | 87 57¼ |
| *ez′* 011 : 301 | 5 | 85 31 —84 7½ | 84 50½ | 84 34¾ |
| *zt′* 031 : 332 | 2 | 44 51 —43 52 | 44 25 | 43 59 |
| *et* 011 : 332 | 1 | 41 2½ | — | 43 45¾ |

*Specific gravity*, determined by floating in Thoulet's solution, 1·177.

*Optical Properties.* A uniaxial figure was obtained on examining the face *c*(001) between crossed Nicols with convergent light. The figure resembled that given by quartz in that it showed circular polarisation. From the figure it was difficult to tell the optical sign, but from other measurements it was deduced to be negative. Approximate values for the refractive indices, determined on a Herbert Smith refractometer, were $\omega = 1{\cdot}66$, $\epsilon = 1{\cdot}61$.

(c) *Chloroform compound* (Fig. 2).

*System*: Anorthic.

*Axial Ratios*: 1·033 : 1 : ?

FIG. 1.

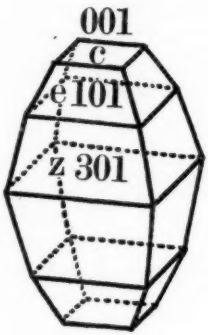
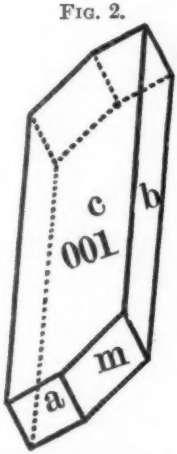



FIG. 2.




*Habit*: The prism zone only was developed, with a large basal plane, and the crystals do not therefore permit calculation of the third axial ratio. Since the crystals were obtained from a solution in which they were very soluble (chloroform and acetone), the faces were always etched, and very bad for measurement. The variations of specific gravity are probably due to gradual loss of chloroform of crystallisation. Many of the crystals seemed to be twins, twin plane probably parallel to *b*(010).

*Forms present*: *a*(100), *b*(010), *c*(001), *m*(110).

| Angles observed. | No. of measurements. | Limits. | Mean observation. | Calculation. |
|---|---|---|---|---|
| $am = 100 : 110$ | 9 | 47° 0′—54° 1′ | 50° 6′ | — |
| $mb = 110 : 010$ | 14 | 42 36—47 36 | 45 28 | — |
| $b'a = 010 : \bar{1}00$ | 18 | 83 0—87 3 | 84 23 | — |
| $a'c = \bar{1}00 : 001$ | 12 | 87 44—89 15 | 88 36 | — |
| $b'c = 0\bar{1}0 : 001$ | 17 | 71 0—74 54 | 73 39 | — |
| $m'c = \bar{1}\bar{1}0 : 001$ | 10 | 75 16—78 31 | 77 7 | 76° 25′ |

*Cleavage*: Very good parallel to *a*(100).

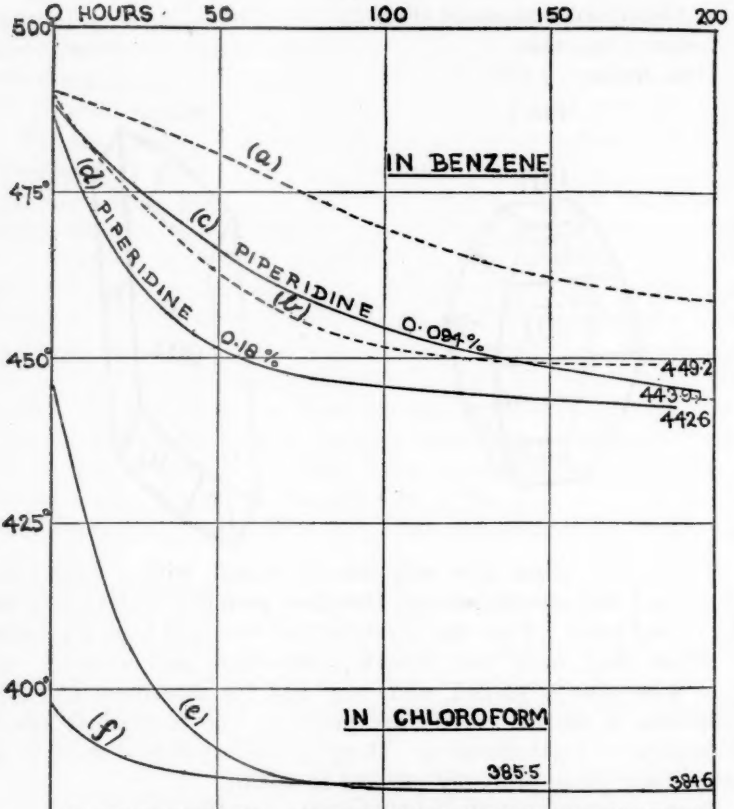
*Specific Gravity*: Determined in Thoulet's Solution.

7 Measurements. Limits 1·317—1·254. Mean 1·284.

8. *Mutarotation.*—The letters below have already been used in Table I and are used again to distinguish the curves of Fig. 3.

(a) and (b) *Mutarotation in benzene.* As the mutarotation (Table II) was very slow, the solution (a) was kept at 20° during the first day, and during each succeeding day, but not during the

FIG. 3.




night; the monomolecular velocity constants for the various days, calculated from the first and last readings taken on that day, show a progressive increase, as if the proportion of catalyst were increasing. After the rotation had become constant, 20 c.c. of this solution were evaporated slowly to dryness, a little acetone was added and evaporated off, and the solid was redissolved in the same volume of benzene. The data given in Table II show that the sample had

## TABLE II.

*Mutarotation of Beryllium Benzoylcamphor in Benzene.*

(*a*) 8 grams per 100 c.c. 6-dcm. tube. $[\alpha] = 2{\cdot}083a$.

| *t*. | $[\alpha]_{5461}$. | $a - x$. | $k$ (hrs.) |
|---|---|---|---|
| 0·5 hr. | 490·15° | 32·31 | |
| 1·1 hrs. | 490·16 | 32·32 | |
| 1·3 ,, | 490·10 | 32·26 | |
| 2·2 ,, | 489·82 | 31·98 | |
| 3·1 ,, | 489·74 | 31·90 | 0·0065 |
| 4·5 ,, | 489·57 | 31·73 | 0·0054 |
| 6·0 ,, | 489·30 | 31·46 | 0·0055 |
| 9·2 ,, | 488·86 | 31·02 | 0·0051 |
| 13·2 ,, | 487·83 | 29·99 | 0·0062 |
| 1 day | 486·34 | 28·50 | 0·0080 |
| 2 days | 481·08 | 23·24 | 0·010 |
| 3 ,, | 475·82 | 17·98 | 0·014 |
| 4 ,, | 470·27 | 12·43 | 0·017 |
| 5 ,, | 466·32 | 8·48 | 0·015 |
| 6 ,, | 462·91 | 5·07 | 0·021 |
| 7 ,, | 460·78 | 2·94 | 0·036 |
| 8 ,, | 458·82 | 0·98 | 0·018 |
| 9 ,, | 457·99 | 0·15 | |
| 10 ,, | 457·84 | | |

After crystallising by slow evaporation and redissolving in the same volume of solvent.

| | | | |
|---|---|---|---|
| 15 mins. | 494·3 | 39·6 | |
| 25 ,, | 494·1 | 39·4 | 0·031 |
| 115 ,, | 492·6 | 37·9 | 0·026 |
| 265 ,, | 489·2 | 37·9 | 0·033 |
| 1137 ,, | 479·5 | 24·8 | 0·025 |
| 1189 ,, | 478·4 | 23·7 | 0·026 |
| 1272 ,, | 477·6 | 22·9 | 0·026 |
| ∞ ,, | 454·7 | | |

(*b*) 9·45 grams per 100 c.c. 6-dcm. tube. $[\alpha] = 1{\cdot}764a$.

| *t* (hrs.). | $[\alpha]_{5461}$. | $a - x$. | $k$ (hrs.). |
|---|---|---|---|
| 2·5 | 485·92° | 36·70 | |
| The iron arc was on for 4½ hours. | | | |
| 28·3 | 471·85 | 22·63 | 0·0187 |
| 29·3 | 471·48 | 22·26 | 0·0186 |
| 30·1 | 470·72 | 21·50 | 0·0193 |
| 33·3 | 469·63 | 20·41 | 0·0190 |
| 46·2 | 464·08 | 14·86 | |
| 48·1 | 463·58 | 14·36 | |
| 50·4 | 462·51 | 13·29 | 0·0280 |
| 52·7 | 461·61 | 12·39 | |
| 56·2 | 460·29 | 11·07 | |
| 71·8 | 456·60 | 7·38 | |
| 72·1 | 456·55 | 7·33 | |
| 74·3 | 456·09 | 6·87 | 0·0398 |
| 75·5 | 455·65 | 6·43 | |
| 80·0 | 454·49 | 5·27 | |
| 81·3 | 454·21 | 4·99 | |
| 122·5 | 449·66 | 0·44 | 0·161 |
| 125·3 | 449·50 | 0·28 | |
| 143·1 | 449·22 | | |

recovered its initial rotatory power, but not its initial purity, since the velocity constant was approximately equal to its final value in the preceding mutarotation. A second curve (b) was obtained from a solution in benzene which had been exposed to the light of an iron arc, passing through the glass discs at the end of the polarimeter tube, during a period of 4½ hours. The velocity constant was increased eight-fold from 0·0055 to 0·044; but since no acceleration was detected in a subsequent experiment, in which a 5 per cent. solution in benzene was exposed to the full action of a mercury arc at a range of about 5 cm. in a silica-jacketed silica polarimeter tube (compare *Trans. Faraday Soc.*, 1913, **9**, 193), the acceleration observed must have been due to the presence in solution (b) of a larger proportion of the casual catalyst, without which mutarotation in an inert solvent would probably be arrested completely.

## TABLE III.

*Mutarotation of Beryllium Benzoylcamphor in Benzene at 20°.*

5 grams per 100 c.c. 2-dcm. tube. [α] = about 10α.

(c) With 0·094% piperidine.

| *t* (mins.). | [α]. | *a* − *x*. | *k*. |
|---|---|---|---|
| 3 | 487·9° | | |
| 4 | 487·6 | 45·0 | |
| 6 | 487·1 | 44·5 | 0·00559 |
| 8 | 486·6 | 44·0 | 0·00561 |
| 12 | 485·2 | 42·6 | 0·00684 |
| 16 | 484·0 | 41·4 | 0·00694 |
| 20 | 482·9 | 40·3 | 0·00689 |
| 28 | 480·7 | 38·1 | 0·00693 |
| 36 | 478·5 | 35·9 | 0·00705 |
| 44 | 476·7 | 34·1 | 0·00693 |
| 52 | 475·0 | 32·4 | 0·00684 |
| 60 | 473·4 | 30·8 | 0·00676 |
| 75 | 470·5 | 27·9 | 0·00669 |
| 90 | 467·8 | 25·2 | 0·00673 |
| 105 | 465·4 | 22·8 | 0·00672 |
| 120 | 463·0 | 20·4 | 0·00681 |
| 135 | 460·9 | 18·3 | 0·00686 |
| 150 | 459·1 | 16·5 | 0·00686 |
| 195 | 454·8 | 12·2 | 0·00683 |
| 215 | 453·9 | 11·3 | 0·00654 |
| 261 | 449·5 | 6·9 | 0·00729 |
| 290 | 448·9 | 6·3 | 0·00687 |
| 320 | 447·8 | 5·2 | 0·00682 |
| 365 | 446·8 | 4·2 | 0·00656 |
| 390 | 444·7 | 2·1 | 0·00794 |
| 470 | 443·7 | 1·1 | 0·00696 |
| | 442·6 | | |
| | | Mean | 0·00684 |

(d) With 0·18% piperidine.

| *t* (mins.). | [α]. | *a* − *x*. | *k*. |
|---|---|---|---|
| 3 | 486·6° | | |
| 4 | 483·4 | 39·5 | |
| 6 | 482·3 | 38·4 | 0·0141 |
| 8 | 481·0 | 37·1 | 0·0157 |
| 10 | 479·9 | 36·0 | 0·0155 |
| 12 | 478·5 | 34·6 | 0·0165 |
| 14 | 477·6 | 33·7 | 0·0159 |
| 16 | 476·3 | 32·4 | 0·0165 |
| 18 | 475·1 | 31·2 | 0·0168 |
| 20 | 474·1 | 30·2 | 0·0168 |
| 22 | 473·1 | 29·2 | 0·0168 |
| 24 | 472·1 | 28·2 | 0·0168 |
| 26 | 471·1 | 27·2 | 0·0169 |
| 28 | 470·3 | 26·4 | 0·0168 |
| 30 | 469·2 | 25·3 | 0·0171 |
| 32 | 468·3 | 24·4 | 0·0172 |
| 36 | 466·7 | 22·8 | 0·0172 |
| 40 | 465·2 | 21·3 | 0·0171 |
| 44 | 463·6 | 19·7 | 0·0174 |
| 48 | 462·3 | 18·4 | 0·0173 |
| 56 | 459·8 | 15·9 | 0·0175 |
| 64 | 458·0 | 14·1 | 0·0172 |
| 73 | 455·8 | 11·9 | 0·0174 |
| 86 | 453·4 | 9·5 | 0·0174 |
| 97 | 451·5 | 7·6 | 0·0177 |
| 112 | 450·4 | 6·5 | 0·0167 |
| 141 | 447·2 | 3·3 | 0·0181 |
| 156 | 446·9 | 3·0 | 0·0169 |
| 246 | 444·6 | 0·7 | 0·0167 |
| | 443·9 | | |
| | | Mean | 0·0169 |

When 0·6 per cent. of benzoic acid was added to an 8 per cent. solution in benzene, a very rapid decrease of rotatory power took place, from $[\alpha]_{5461} = 490{\cdot}1°$ to 425·7°, a change of 64·4° in about 5 hours; but, since the final rotatory power was much lower than usual, it was certain that the benzoic acid had decomposed the beryllium compound, in addition to catalysing the mutarotation. If the benzoic acid had reacted completely with the beryllium compound to form benzoylcamphor and beryllium benzoate, the consequent loss of rotation would have been 32·4°; the mutarotation of the remaining beryllium compound (0·8 of the total quantity) would account for a further fall of $0{\cdot}8 \times 39{\cdot}4 = 31{\cdot}5°$, which agrees very closely with the difference of $64{\cdot}4° - 32{\cdot}4° = 32°$ actually observed.

(c) and (d) *Mutarotation in benzene in presence of piperidine.* The data for two concentrations of piperidine are given in Table III.

TABLE IV.

*Mutarotation of Beryllium Benzoylcamphor in Chloroform at* 20°.

(*e*) 9·66 grams per 100 c.c. 2-dcm. tube. $[\alpha] = 5{\cdot}174\alpha$.

| *t* (mins.). | $[\alpha]_{5461}$. | $a - x$. | *k*. |
|---|---|---|---|
| 10 | 436·1 | 51·5 | |
| 17 | 429·4 | 44·8 | 0·0199 |
| 22 | 424·7 | 40·1 | 0·0209 |
| 27 | 419·9 | 35·3 | 0·0223 |
| 32 | 415·7 | 31·1 | 0·0229 |
| 37 | 412·7 | 28·1 | 0·0224 |
| 42 | 409·4 | 24·8 | 0·0228 |
| 47 | 406·8 | 22·2 | 0·0228 |
| 52 | 404·0 | 19·4 | 0·0232 |
| 57 | 402·3 | 17·7 | 0·0227 |
| 67 | 398·5 | 13·9 | 0·0229 |
| 77 | 395·7 | 11·1 | 0·0229 |
| 99 | 391·0 | 6·4 | 0·0233 |
| 111 | 389·1 | 4·5 | 0·0241 |
| 121 | 388·0 | 3·4 | 0·0244 |
| 134 | 387·0 | 2·4 | 0·0245 |
| 166 | 385·8 | 1·2 | 0·0243 |
| 193 | 385·1 | 0·5 | 0·0248 |
| 227 | 384·8 | 0·2 | 0·0251 |
| 356 | 384·6 | | |
| | | Mean | 0·0231 |

(*f*) 15 grams of chloroform-compound (= 10·28 grams of beryllium benzoylcamphor) per 100 c.c. 2-dcm. tube. $[\alpha] = 4{\cdot}864\alpha$.

| *t* (mins.). | $[\alpha]_{5461}$. | $a - x$. | *k*. |
|---|---|---|---|
| 11 | 394·5 | 9·0 | |
| 38 | 390·2 | 4·7 | 0·0240 |
| 45 | 389·8 | 4·3 | 0·0217 |
| 55 | 388·8 | 3·3 | 0·0228 |
| 60 | 388·5 | 3·0 | 0·0224 |
| 70 | 387·9 | 2·4 | 0·0224 |
| 80 | 387·4 | 1·9 | 0·0225 |
| 100 | 386·8 | 1·3 | 0·0217 |
| 133 | 386·0 | 0·5 | 0·0237 |
| 163 | 385·6 | 0·1 | 0·0296 |
| 261 | 385·5 | | |
| | | Mean | 0·0227 |

The constancy of the velocity constant throughout the change shows that the action is certainly monomolecular. The great catalytic effect of piperidine is shown by the fact that the velocity of change was increased about 70-fold, from 0·0055 to 0·41 per hour, by the addition of less than 1 part in 1000 of piperidine.

(e) and (f) *Mutarotation in chloroform.* The mutarotation of the parent substance and of its chloroform compound in an approximately 10 per cent. solution in chloroform is shown in Table IV. *The velocity constant is almost identical in the two cases,* although the initial value of the rotation is very much lower in the case of the chloroform compound than in that of the parent substance. The rate of change is approximately 250 times as great as in benzene.

(g) *Mutarotation in acetone.* The data in Table V give a steady value for the monomolecular constant, but this is 600 times greater than for the purer of the two solutions in benzene (curve *a*), showing that acetone is an even more active catalyst than chloroform.

(h) *Mutarotation in alcohol.* No mutarotation curve was plotted, but it was found that at the end of ½ hour the solubility of beryllium benzoylcamphor had almost reached its maximum value, showing

that the change had proceeded very rapidly in this solvent also. Only the final rotatory power is shown in Table I.

(i) and (j) *Heptane and* cyclo*Hexane.* The data in Table VI were observed in solutions which had been almost saturated by shaking with the solvent for two minutes, and were then filtered. The limiting values are practically identical in these two solvents. As in the case of benzene, the mutarotation in these hydrocarbon solvents probably depends on the presence of a casual catalyst; the unequal velocity constants in the two solvents are therefore attributed to their unequal contamination, rather than to any fundamental difference in their catalytic activity, which would probably be negligible in both solvents, if pure.

## TABLE V.

*Mutarotation of Beryllium Benzoylcamphor in Acetone at* 20°.

(*g*) 1·639 grams per 100 c.c. 2-dcm. tube. $[\alpha] = 31{\cdot}2a$.

| $t$ (mins.). | $[\alpha]$. | $a - x$. | $k$. | $t$ (mins.). | $[\alpha]$. | $a - x$. | $k$. |
|---|---|---|---|---|---|---|---|
| 3 | 425·5 | 42·5 | | 27 | 394·1 | 11·1 | 0·056 |
| 5 | 421·9 | 38·9 | 0·044 | 33 | 390·8 | 7·8 | 0·056 |
| 7 | 417·9 | 34·9 | 0·049 | 39 | 388·0 | 5·0 | 0·059 |
| 9 | 414·2 | 31·2 | 0·052 | 47 | 386·2 | 3·2 | 0·059 |
| 11 | 410·9 | 27·9 | 0·053 | 55 | 385·0 | 2·0 | 0·059 |
| 15 | 405·1 | 22·1 | 0·054 | 70 | 383·8 | 0·8 | 0·059 |
| 19 | 400·8 | 17·8 | 0·054 | 101 | 383·0 | | |
| 23 | 396·9 | 13·9 | 0·056 | | | Mean | 0·056 |

## TABLE VI.

*Mutarotation of Beryllium Benzoylcamphor at* 20°.

(*i*) In heptane, 0·240 gram per 100 c.c. 2-dcm. tube. $[\alpha] = 208a$.

| $t$ (mins.). | $[\alpha]$. | $a - x$. | $k$. |
|---|---|---|---|
| 4 | 425° | 50 | |
| 5 | 425 | 50 | |
| 7 | 423 | 48 | 0·020 |
| 9 | 421 | 46 | 0·021 |
| 13 | 419 | 44 | 0·016 |
| 21 | 410 | 35 | 0·022 |
| 23 | 408 | 33 | 0·023 |
| 40 | 402 | 27 | 0·018 |
| 72 | 392 | 17 | 0·016 |
| 115 | 385 | 10 | 0·015 |
| 165 | 381 | 6 | 0·013 |
| 175 | 0·03% of piperidine added. | | |
| 177 | 375 | Mean | 0·018 |

(*j*) In *cyclo*hexane, 0·561 gram per 100 c.c. 2-dcm. tube. $[\alpha] = 89a$.

| $t$ (mins.). | $[\alpha]$. | $a - x$. | $k$. |
|---|---|---|---|
| 19 | 424° | 53 | |
| 23 | 423 | 52 | 0·0048 |
| 27 | 423 | 52 | 0·0024 |
| 40 | 421 | 50 | 0·0028 |
| 62 | 419 | 48 | 0·0023 |
| 137 | 415 | 44 | 0·0016 |
| 170 | 411 | 40 | 0·0019 |
| 218 | 409 | 38 | 0·0017 |
| 261 | 407 | 36 | 0·0016 |
| 306 | 405 | 34 | 0·0016 |
| | | Mean | 0·0020 |
| 310 | 0·03% of piperidine added. | | |
| 312 | 394 | 23 | 0·0029 |
| 316 | 383 | 12 | 0·0050 |
| 322 | 377 | 6 | 0·0072 |
| 406 | 371 | 0 | |

9. *Solubility.*—Observations of the concentration and rotatory power of saturated solutions in heptane and in *cyclo*hexane at 20° were made in order to deduce values for the proportion of the original form in the equilibrium mixture and for the rotatory power of its labile isomeride. The methods were similar to those already used in the case of nitrocamphor and the sugars (*J.*, 1904, **85**, 1541, 1551). Samples of the saturated solutions were taken at 5, 15, 20, and 40 minutes; but since the five-minute samples were obviously not saturated, they were only used for the determinations of initial rotatory power which are recorded in Table I, the initial solubilities being deduced by extrapolation to zero time from the other values. The principal results are shown in Table VII.

TABLE VII.

*Concentration and Rotatory Power of Saturated Solutions of Beryllium Benzoylcamphor in Heptane and in* cyclo*Hexane at* 20°.

| | | Concentration of saturated solutions. | | | | Specific rotations of saturated solutions. | | | | | | Percentage of the original form in the equilibrium mixture. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Grams per 100 grams of solvent. | | Grams per 100 c.c. of solution. | | Original form. | | Mixture. | | Predicted rotation for the new form. | | |
| Solvent. | Catalyst. Piperidine. | Original form. | Mixture. | Original form. | Mixture. | $[\alpha]_{5461}$. | $[\alpha]_{5780}$. | $[\alpha]_{5461}$. | $[\alpha]_{5780}$. | $[\alpha]_{5461}$. | $[\alpha]_{5780}$. | |
| Heptane. | 0·038% | 0·272 | 0·609 | 0·195 | 0·438 | 446° | 371° | 374° | 311° | (<316°) | (<263°) | (>45) |
| *cyclo*-Hexane. | 0·038% | 0·600 | 1·617 | 0·460 | 1·240 | 450 | 367 | 372 | 309 | (<326) | (<275) | (>37) |
| | Mean or corrected values | | | | | 448 | 369 | 373 | 310 | 292 | 246 | 48 |

The concentration ratios in the table were not corrected for the influence of the labile isomeride on the solubility of the more stable form of the compound. The proportions shown in the last column are therefore minimum values. Since the observed rotations, both of the initial compound and of the final equilibrium mixture, are practically identical in the two solvents, it is unlikely that the equilibrium proportions differ substantially. The lower ratio in *cyclo*hexane is therefore probably due, at least in part, to the fact that the solubilities in this solvent are $2\frac{1}{2}$ times as great as in heptane. A proportional correction applied to the ratio in heptane would raise it to 48 per cent., so that the proportion of the stable and labile isomerides must be at least very nearly, even if not exactly, equal to unity.

10. *Freezing points.*—A solution of 1·173 gms. of beryllium benzoylcamphor in 44·596 gms. of benzene showed initially a depression of the freezing point of 0·278°, whilst a week later the depression was 0·285°. The molecular weights deduced from these data are below the theoretical figures, but it is clear that the mutarotation is not accompanied by any important change of molecular weight.

11. *Summary.*

(*a*) A new method of preparing co-ordination compounds with the help of piperidine is described.

(*b*) Crystallographic details are given of a tetragonal form of beryllium benzoylcamphor, and of an anorthic compound with 2 mols. of chloroform.

(*c*) When the tetragonal crystals are dissolved, a slow mutarotation is observed in benzene and a very rapid mutarotation in acetone or chloroform. This is attributed to a reversal of sign in the rotatory power of an optically active beryllium complex.

(*d*) Observations of freezing point show that the stable and labile forms of the compound are isomeric, and measurements of solubility show that they are present in approximately equal proportions when equilibrium is reached. Estimates are given of the probable rotatory power of the labile form and of the partial rotation of the beryllium.

(*e*) Although it presents many points of analogy with the behaviour of nitrocamphor and the sugars, the mutarotation of beryllium benzoylcamphor is fundamentally different in that it is accelerated by chloroform as well as by piperidine and benzoic acid. The chloroform compound, the rotatory power of which does not differ much from that of the equilibrium mixture, is regarded as an intermediate phase in the isomeric change when brought about by this catalyst.

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## CCLXXIV.—*An Apparatus for the Viscosimetric Determination of Transition Points.*

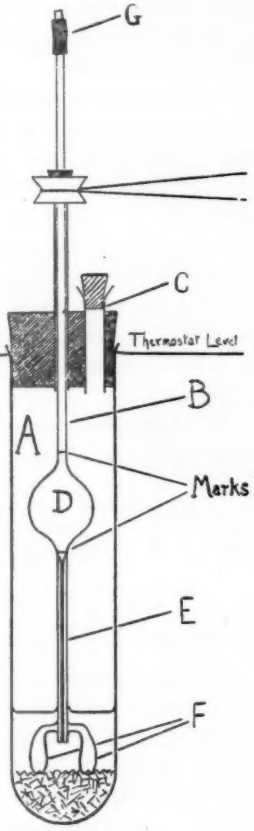
By NORMAN HOLT HARTSHORNE.

DUNSTAN and LANGTON (J., 1912, **101**, 418) determined the transition points of a number of salts by preparing saturated solutions at different temperatures and measuring their times of flow in a viscosimeter of the Ostwald type. In the apparatus now described, successive solutions are prepared and their times of flow determined in one and the same vessel, thereby effecting a considerable saving of time.

The apparatus (Fig. 1) consists of a solubility tube, *A*, 25 cm. long and 5 to 6 cm. wide, fitted with a rubber bung carrying a combined viscosimeter and stirrer, *B*, and a wide tube, *C*, which

normally is closed with a cork. The bulb, *D*, of the viscosimeter has a capacity of about 20 c.c. The capillary, *E*, is 10 cm. long, and its bore is varied to suit the nature of the substance to be examined; in the present work, about 0·75 mm. was found to be suitable, and this would probably be so for all salts of average solubility. Glass paddles, *F*, are sealed on the capillary about 0·5 cm. from the end.

FIG. 1.




To carry out a determination, about 80 c.c. of the saturated solution together with excess salt are placed in *A* and the apparatus is fitted together and immersed in a glass-sided thermostat (regulated to $\pm 0{\cdot}02°$). The viscosimeter, closed by a rubber cap, *G*, to exclude dust, is rotated until equilibrium is reached, the solid is allowed to settle completely, and *G* is replaced by a piece of rubber tubing by means of which solution is sucked up beyond the higher mark. The viscosimeter is raised clear of the remaining liquid, and its contents are allowed to drop back, the time of flow from the upper to the lower mark being noted. After a duplicate reading has been made in the same way, the viscosimeter is washed down with distilled water (2 c.c.), *G* is replaced, and the solution stirred again at another temperature. By means of additions or withdrawals through the tube *C*, the quantities of solid and solution can be adjusted when necessary. The time taken to reach equilibrium can readily be determined by taking readings at the same temperature until the results are constant. In the present work, 6 hours were usually found to be sufficient, but in most cases 12 to 24 hours were allowed.

The following transition points have been determined :—

$$Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4+10H_2O.$$
$$NiSO_4,7H_2O \rightleftharpoons NiSO_4,6H_2O(blue)+H_2O.$$
$$Na_2HPO_4,12H_2O \rightleftharpoons Na_2HPO_4,7H_2O + 5H_2O.$$

The results are given below, the time of flow being recorded in seconds.

### *Sodium Sulphate.*

$Na_2SO_4,10H_2O$. 20·0°, 133; 22·7°, 140; 23·0°, 142; 24·2°, 144; 26·5°, 156; 26·7°, 157; 29·6°, 174; 30·5°, 184; 32·5°, 219; 32·6°, 221; 32·7°, 225.

$Na_2SO_4$. 25·1°, 289; 26·1°, 277; 31·0°, 232; 32·0°, 225; 32·8°, 219; 33·2°, 215; 33·8°, 214; 34·8°, 205; 35·0°, 205; 35·9°, 198; 36·8°, 192; 38·4°, 183.

### *Nickel Sulphate.*

$NiSO_4,7H_2O$. 21·4°, 355; 24·5°, 350; 27·0°, 347; 27·7°, 347; 28·1°, 347; 31·4°, 347; 34·3°, 347.

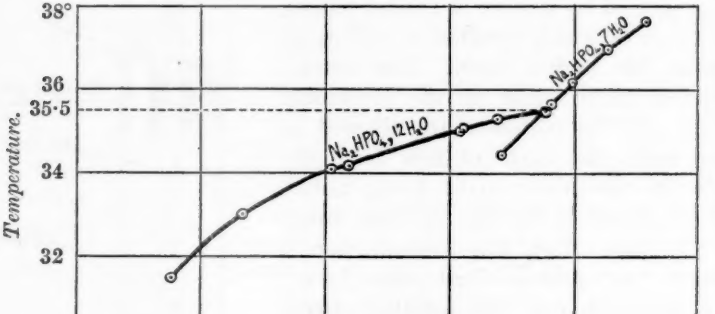
$NiSO_4,6H_2O$ (blue). 25·1°, 367; 25·8°, 361; 27·0°, 356; 29·1°, 349; 29·8°, 345; 30·1°, 343; 30·6°, 342; 32·1°, 336; 33·7°, 331; 34·5°, 329.

### *Disodium hydrogen phosphate.*

$Na_2HPO_4,12H_2O$. 31·5°, 166; 33·0°, 200; 34·1°, 243; 34·2°, 252; 35·0°, 305; 35·05°, 306; 35·3°, 323; 35·5°, 346.

$Na_2HPO_4,7H_2O$. 34·45°, 325; 35·65°, 349; 36·2°, 359; 36·95°, 377; 37·65°, 395.

FIG. 2.




In the experiments with sodium sulphate and nickel sulphate the temperature regulation was not so sensitive as is desirable and the results when plotted show small irregularities. The transition points deduced from them are 32·55° for sodium sulphate (Richards and Wells, *Z. physikal. Chem.*, 1903, **43**, 471, found 32·383° on the hydrogen scale, whilst Berkeley, *Phil. Trans.*, 1904, **203**, [*A*], 209, and Gay-Lussac, *Ann. chim. phys.*, 1819, **11**, 312, found 32·5°) and 29·3° for nickel sulphate (Steele and Johnson, J., 1904, **85**, 113, found 31·5°). The low result in the case of nickel sulphate is attributed to impurity.

In the case of disodium hydrogen phosphate, the temperature was regulated to within $\pm$ 0·02° and the curve (Fig. 2) is markedly more regular. The transition point obtained is 35·5°. Values given by previous workers are 36·4° (Person, *Ann. chim. phys.*,

1849, [iii], **27**, 253), 35·0° (Tilden, J., 1884, **45**, 268), *ca.* 36·6° (Baur, *Z. physikal. Chem.*, 1895, **18**, 180), and 35·4° (D'Ans and Schreiner, *ibid.*, 1911, **75**, 99). The value obtained is thus in good agreement with the latest work. The salt used was B.D.H. ordinary reagent and was twice recrystallised, the crystals being washed with ice-water.

The reproducibility of the curves was shown by repeating portions of them; the figures so obtained are included in those given above. Duplicate readings were taken at all temperatures and never varied by more than 1 second, the agreement being usually within 0·5 second. Failure to reach this points to an obstruction in the capillary tube, which sometimes occurs when the viscosimeter has not been washed. A less frequent cause is the presence of dust in the solution, which should therefore be filtered before being poured into the apparatus. For a similar reason, it is better not to dry the solids with filter-paper after recrystallisation. In all cases except one, in which the solution contained a considerable quantity of filter-paper dust, it was found quite easy to clear the tube *in situ* with a little distilled water. The close agreement between duplicate readings shows that this plan of washing with water has no appreciable effect on the accuracy of the method.

The apparatus in its present form is not suitable for salts giving volatile products of hydrolysis, *e.g.*, sodium carbonate, which lost carbon dioxide on prolonged stirring, but could probably be made so by the addition of a mercury seal.

In conclusion, I desire to express my thanks to Dr. J. F. Spencer for his helpful interest in this work.

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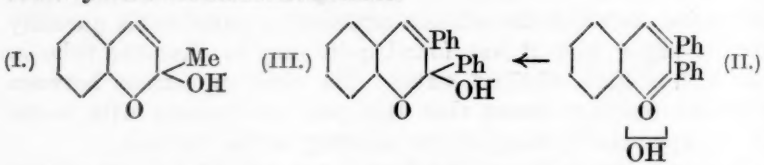
# CCLXXV.—*The Isomerism of the Styryl Alkyl Ketones. Part I. The Isomerism of 2-Hydroxystyryl Methyl Ketone.*

By ALEXANDER MCGOOKIN and ISIDOR MORRIS HEILBRON.

2-HYDROXYSTYRYL methyl ketone was first described by Tiemann and Kees (*Ber.*, 1885, **18**, 1955) as colourless needles (m. p. 139°) obtained by the condensation of helicin with acetone and hydrolysis of the glucoside derivative. Harries (*Ber.*, 1891, **24**, 3180) next prepared this compound by condensation of salicylaldehyde with acetone in presence of dilute alkali. The colour of the purified

compound was not described but, according to this author, the ketone yielded an intense yellowish-red sodium salt. We have found that the ketone prepared according to this method, if precipitated by carbon dioxide, can be directly crystallised from benzene, yielding pale yellow leaflets (m. p. 139°).* Buck and Heilbron (J., 1922, **121**, 1095) observed that, although this yellow ketone failed to condense with gentisaldehyde, it nevertheless underwent change, being recovered in the colourless form described by Tiemann and Kees. The present investigation was undertaken in order to establish the exact structure of this colourless isomeride, which was first assumed to have the constitution (I) owing to the fact that, whereas the ordinary yellow 2-hydroxystyryl methyl ketone gave a bright crimson solution with aqueous sodium hydroxide, the colourless isomeride yielded only a pale yellow solution, a peculiarity which appeared inexplicable if the two forms were actually *cis-trans*-stereoisomerides.




That ring-chain tautomerism of the above type is possible has been fully demonstrated by Decker and Becker (*Ber.*, 1922, **55**, 375), who obtained the colourless carbinol (III) from 2 : 3-diphenylphenopyrylium hydroxide (II). Attempts were first made to synthesise from coumarin, by means of the Grignard reaction, either 2-methylphenylpyranol or its methyl ether, but these proved fruitless, although the corresponding pyrylium ferrichloride was readily obtained (compare Decker and Fellenberg, *Annalen*, 1907, **356**, 295). Assuming that the colourless modification has the carbinol constitution, it should be possible to methylate it by boiling in methyl-alcoholic solution, a reaction which Decker and Becker (*loc. cit.*) found to take place readily in the case of 2 : 3-diphenylphenopyranol. Methylation in this manner completely failed, but with methyl sulphate, a methyl ether was obtained identical with that formed from the yellow isomeride. It would thus appear that the two modifications are in reality stereoisomerides. That, moreover, a ketonic group is present in the molecule of the colourless form was shown by the preparation of an oxime, semicarbazone, and phenylhydrazone, each being identical with

* Specimens of this compound obtained both from The British Drug Houses, Ltd., and from Professor F. J. Wilson in Glasgow were of similar colour and gave red solutions when treated with alkali.

the analogous derivative obtained from the yellow isomeride. As a crucial test, attention was next turned to β-hydroxy-β-3-methoxy-2-hydroxyphenylethyl methyl ketone (Heilbron and Whitworth, J., 1923, **123**, 238), which compound cannot exhibit *cis-trans*-isomerism but could obviously rearrange to form the ring pyranol. Under no conditions, however, was a colourless modification of this aldol obtained, and it may be concluded that the two forms of 2-hydroxystyryl methyl ketone are actually *cis-trans*-isomerides. The only other case recorded of isomerism in similar ketones is with 4 : 5-methylenedioxystyryl methyl ketone, which Haber (*Ber.*, 1891, **24**, 617) obtained in a colourless form (m. p. 111°) and a yellow form (m. p. 107°). On repeating this work, we have found that actually both forms melt sharply at 110—111°. In every case where isomeric styryl ketones have been obtained, both isomerides have invariably identical m. p.'s, and it is evident that one isomeride passes into the other at or just below the melting point. As regards configuration, the yellow isomeride must represent the *cis*-form, since it immediately yields a pyrylium-salt coloration with concentrated hydrochloric acid, whereas the colourless isomeride only does so after prolonged heating.

In addition to having prepared the colourless 2-hydroxystyryl methyl ketone, we have isolated colourless modifications of 5-bromo-2-hydroxystyryl methyl ketone and 3-methoxy-4-hydroxystyryl methyl ketone. Other ketones are at present under examination.

In connexion with the difference in colour produced by the addition of alkali to the two modifications, the attempted preparation of the sodium salt of the yellow isomeride led to entirely unexpected results. On treating a solution of this in absolute alcohol with the requisite quantity of alcoholic sodium ethoxide, the usual crimson coloration was produced, and from the solution, on fractional precipitation with chloroform, dark crimson crystals having a green metallic lustre separated. These proved to be the sodium salt of 2 : 2′-dihydroxydistyryl ketone, from which the free ketone was isolated on acidification. On the further addition of chloroform to the filtrate, orange-coloured crystals separated which yielded, after crystallisation from absolute alcohol and rendering acid, the pure colourless isomeride. Further fractionation of the original filtrate with chloroform precipitated a golden-coloured and, finally, a pale yellow salt. The former was the pure sodium salt corresponding to the colourless isomeride, and the latter the sodium derivative of salicylaldehyde. The presence of this accounts for the formation of the dihydroxydistyryl ketone, which could only have resulted through a partial disruption of the yellow isomeride into salicylaldehyde and acetone in the presence

of alkali followed by recondensation of the components to the distyryl ketone. These results confirm the observations made by Heilbron and Buck (J., 1921, **119**, 1500), who, however, employed aqueous alkali to bring about the fission of various substituted styryl methyl ketones. By using aqueous alkali in place of alcoholic sodium ethoxide, acetone has been identified in addition to the above-mentioned fission products. Whether the orange salt corresponds to the yellow isomeride is uncertain. From the evidence before us, it seems clear that, as ordinarily prepared, 2-hydroxystyryl methyl ketone is a mixture of both isomerides in which the yellow *cis*-modification is labile and disrupts in presence of alkali. On the other hand, the colourless variety readily forms a sodium salt and only yields 2 : 2′-dihydroxydistyryl ketone on heating of the alkaline solution.

## EXPERIMENTAL.

*Colourless 2-hydroxystyryl methyl ketone* (*trans*-isomeride) was prepared from the yellow form in the way described by Buck and Heilbron (*loc. cit.*). Besides gentisaldehyde, protocatechualdehyde, *p*-hydroxybenzaldehyde, and vanillin were also employed and, in each case, the colourless modification was obtained. The purest product resulted from the vanillin reaction (yield nearly theoretical).

The isomerisation of the yellow into the colourless form can also be accomplished by boiling in benzene, toluene, amyl alcohol, or acetoacetic ester solution, especially in presence of a trace of dry hydrogen chloride; and also by boiling the yellow form with water, when some of it dissolves and a dark oil appears; the decanted clear aqueous solution, on cooling, deposits prismatic crystals of a faintly green colour which can readily be obtained absolutely colourless by recrystallisation from benzene. From his method of preparation, Harries (*loc. cit.*) must have obtained mainly the colourless isomeride, although the formation of the yellow-red sodium salt indicates that isomerisation could not have been complete. Finally, exposure of an alcoholic solution of the yellow form to light of short wave-length from a quartz mercury lamp for 24 hours resulted in complete isomerisation (Found in specimen from vanillin reaction, C = 74·0; H = 6·4. Calc., C = 74·1; H = 6·2%).

2 : 2′-*Dihydroxydistyryl Ketone from the Colourless Isomeride.*—A mixture of the colourless isomeride (4 gms.), salicylaldehyde (3 gms.), and sodium hydroxide (30 c.c. of 10%) was left for 3 days and was then carefully neutralised with dilute hydrochloric acid. The brown precipitate, twice crystallised from benzene, gave yellow needles of 2 : 2′-dihydroxydistyryl ketone (m. p. 159°).

Decker and Felser (*Ber.*, 1908, **41**, 3005) give m. p. 168°, but the compound has repeatedly been prepared in these laboratories and no specimen has ever been obtained melting above 159°.

The dark green crystals obtained on keeping the filtrate from the distyryl ketone melted, after purification, at 100° and were identified as diphenospiropyran (Decker and Felser, *loc. cit.*). When the pure colourless modification of 2-hydroxystyryl methyl ketone is dissolved in excess of alkali, no red coloration is produced even on prolonged standing. On heating the solution, however, the red coloration characteristic of the sodium derivative of the distyryl ketone immediately makes its appearance; on cooling, green lustrous crystals of the sodium derivative of 2 : 2′-dihydroxydistyryl ketone separate.

*Oxime from either Isomeride.*—The following method of formation is more satisfactory than that employed by Harries (*loc. cit.*). A mixture of 2-hydroxystyryl methyl ketone (5 gms. in alcohol) and aqueous hydroxylamine acetate (from 2 gms. of hydrochloride) was boiled for 2 hours on a water-bath, the alcohol removed, and the oxime extracted with ether and crystallised from benzene, when colourless nodules (m. p. 84°) were obtained (Found : N = 7·8. Calc., N = 7·9%).

The *phenylhydrazone* prepared from either isomeride by the action of phenylhydrazine acetate crystallised from benzene in bright yellow crystals (m. p. 159°) and was identical with the phenylhydrazone obtained by Harries (*loc. cit.*). On crystallisation of the phenylhydrazone from boiling alcohol, greenish-yellow crystals of 1-phenyl-5-*o*-hydroxyphenyl-3-methylpyrazoline were obtained, m. p. 147—148° (compare Auwers and Müller, *Ber.*, 1908, **41**, 4230) (Found : C = 76·0; H = 6·4; N = 11·3. Calc., C = 76·1; H = 6·4; N = 11·1%).

*Semicarbazone of 2-Hydroxystyryl Methyl Ketone.*—Both isomerides yielded the same semicarbazone, which was prepared by Borsche and Merkwitz's method (*Ber.*, 1904, **37**, 3184).

*2-Methoxystyryl Methyl Ketone from the Colourless Isomeride.*—This compound, first obtained by Heilbron and Buck (J., 1921, **119**, 1509) from the yellow isomeride of 2-hydroxystyryl methyl ketone by methylation with methyl sulphate, and now prepared from the colourless isomeride by the action of methyl iodide and dry silver oxide, was, however, most conveniently produced by boiling a solution of the pure sodium salt (6 gms.) in methyl alcohol and methyl iodide (10 gms.) until the colour of the solution was entirely discharged, removing the excess of methyl iodide, and adding water to the residue; the oil which separated was taken up in alcohol and allowed to crystallise (m. p. 50°).

*Sodium Salt of Yellow 2-Hydroxystyryl Methyl Ketone.*—The

yellow isomeride (14 gms.) dissolved in absolute alcohol, was treated with the requisite quantity of sodium ethoxide solution; a few c.c. of chloroform were then added. The crystalline deposit that gradually formed was recrystallised from absolute alcohol, when lustrous, bottle-green crystals were produced (3 gms.). On acidification, the dark crimson aqueous solution furnished yellow 2 : 2′-dihydroxydistyryl ketone, m. p. 159° after purification.

On fractionally precipitating the alcoholic filtrate by means of chloroform, an orange salt (2·8 gms.) and a golden-coloured salt (3 gms.) were obtained, both of which dissolved in water to give yellow solutions. In the case of the orange crystals, a yellow precipitate, which immediately turned colourless, was formed on rendering the solution acid. After recrystallisation from benzene, this melted at 139° and was identified as colourless 2-hydroxystyryl methyl ketone. It is possible that the yellow precipitate which was first produced was actually the yellow *cis*-isomeride and that the orange salt corresponds to this modification.

In addition to the salts described above, salicylaldehyde was found in the acidified residual solution.

*Sodium Salt of Colourless 2-Hydroxystyryl Methyl Ketone.*—The colourless isomeride (7 gms.), dissolved in absolute alcohol, was treated with sodium ethoxide solution (1 gm. of sodium). On addition of chloroform golden-coloured crystals separated.

*5-Bromo-2-hydroxystyryl Methyl Ketone.*—The yellow form of this compound was obtained by Heilbron and Whitworth's method (*loc. cit.*). On attempting to condense this compound with protocatechuic and other aldehydes, the colourless isomeride was obtained, needles, m. p. 154°. No depression in melting point occurred when these two isomerides were melted together (Found : C = 49·6; H = 3·8. $C_{10}H_9O_2Br$ requires C = 49·8; H = 3·7%).

*3-Methoxy-4-hydroxystyryl Methyl Ketone.*—The yellow modification of this compound was produced by Heilbron and Forster's method (this vol., p. 340) and converted into the colourless isomeride by the methods already detailed. It crystallises in needles; m. p. 129°, which is also the m. p. of a mixture of both forms (Found : C = 68·9; H = 6·2. Calc., C = 68·8; H = 6·2%).

*4 : 5-Methylenedioxystyryl Methyl Ketone.*—This compound was described by Haber (*loc. cit.*) as a yellow modification of m. p. 107° and a colourless form (m. p. 111°). After repeated crystallisation of the yellow form from alcohol and of the colourless from water, both isomerides have been obtained melting at 110—111°.

In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a

grant to one of us (A. McG.) which has enabled this work to be carried out, and also to Professor F. J. Wilson for kindly preparing 2-hydroxystyryl methyl ketone.

THE UNIVERSITY, LIVERPOOL. [*Received, June 19th*, 1924.]

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## CCLXXVI.—*Elimination of the Amino-group of Tertiary Amino-alcohols. Part II. The Semipinacolinic Deamination of β-Hydroxy-αβ-diphenyl-β-naphthylethylamine.*

By ALEX. MCKENZIE and WALTER SAMUEL DENNLER.

IN the course of a previous research (McKenzie and Richardson, J., 1923, **123**, 79) the observation was made that the action of nitrous acid on β-hydroxy-αβ-diphenyl-β-naphthylethylamine took an unexpected course inasmuch as it did not proceed on the lines :

$$C_{10}H_7\cdot CPh(OH)\cdot CHPh\cdot NH_2 \longrightarrow C_{10}H_7\cdot CPh(OH)\cdot CHPh\cdot OH.$$

Instead of naphthylhydrobenzoin, a compound, $C_{24}H_{18}O$, was isolated and the conclusion was arrived at that this compound was either naphthyldeoxybenzoin or one of its isomerides. One of the objects of the work now described was to determine the constitution of this compound, and to find out if its formation was to be attributed to semipinacolinic deamination.

Of the seven possibilities, VI and VII may at once be disregarded,

(I.) $C_{10}H_7\cdot CPh_2\cdot CHO$ (II.) $C_{10}H_7\cdot CHPh\cdot COPh$

(III.) $CHPh_2\cdot CO\cdot C_{10}H_7$ (IV.) $C_{10}H_7\cdot \overset{O}{\overset{\diagup\diagdown}{CPh}}\cdot CHPh$

(V.) $\overset{O}{\overset{\diagup\diagdown}{CPh_2}}\cdot CH\cdot C_{10}H_7$ (VI.) $CPh_2{:}C(OH)\cdot C_{10}H_7$

(VII.) $C_{10}H_7\cdot CPh{:}CPh\cdot OH$

especially in the light of the recent conclusions arrived at respecting the constitution of phenyldeoxybenzoin (Meyer and Gottlieb-Billroth, *Ber.*, 1921, **54**, [*B*], 575; McKenzie and Boyle, J., 1921, **119**, 1131; Ley and Manecke, *Ber.*, 1923, **56**, [*B*], 777).

Incidentally to our purpose it was thus desirable that a study of the dehydration of α-naphthylhydrobenzoin should be made in some detail.

McKenzie and Roger (this vol., p. 844) obtained diphenylnaphthylethylenic oxide (m. p. 180—181°) by the action of dilute sulphuric acid on α-naphthylhydrobenzoin, whilst the use of con-

centrated sulphuric acid led to the formation of the compound prepared by McKenzie and Richardson by a different method. We have now found that with hot dilute sulphuric acid both diphenylnaphthylacetaldehyde (I) and α-naphthyldeoxybenzoin (II) are produced in addition to the ethylenic oxide. The solid which was separated from the benzene mother-liquors in the above dehydration melted indefinitely, and was obviously a mixture. When it was hydrolysed by alcoholic potash the presence of four decomposition products was proved, namely, formic acid, benzoic acid, phenylnaphthylmethane, and diphenylnaphthylmethane. The formation of benzoic acid and phenylnaphthylmethane would indicate that the following disruption had occurred:

$$C_{10}H_7\cdot CPhH\text{–}\vdots\text{–}COPh$$
$$H\text{–}\vdots\text{–}OH$$

whilst the formation of formic acid and diphenylnaphthylmethane would indicate $C_{10}H_7\cdot CPh_2\text{–}\vdots\text{–}CHO$ / $H\text{–}\vdots\text{–}OH$.

The separation of the α-naphthyldeoxybenzoin, which is the main constituent of the above mixture, presented difficulties, but was eventually accomplished. This compound (m. p. 109—110°) is naphthyldeoxybenzoin (II), but the issue was rendered complicated because the isomeride of McKenzie and Richardson, which is also produced in the dehydration of the glycol with concentrated sulphuric acid, melts at about the same temperature, namely 108—109°. The two isomerides, however, show a very marked depression of melting point on admixture, have a different crystalline appearance, and give a somewhat different colour reaction with concentrated sulphuric acid.

The compound, m. p. 108—109°, is diphenylacetonaphthone, and its constitution was established in two ways from diphenylacetyl chloride, (*a*) by aluminium chloride and naphthalene, and (*b*) by magnesium α-naphthyl bromide. Further evidence was afforded by its behaviour with alcoholic potash, when α-naphthoic acid was identified as one of the products, and by its behaviour on oxidation, when benzophenone was formed.

Diphenylacetonaphthone is not the sole product of the dehydration of naphthylhydrobenzoin with concentrated sulphuric acid, as the oil from which the naphthone had been partly separated consisted mainly of α-naphthyldeoxybenzoin, m. p. 109—110°.

The dehydration of α-naphthylhydrobenzoin exemplifies the various types of action according to the ideas of Tiffeneau and his colleagues (*Bull. Soc. chim.*, 1923, [iv], **33**, 759 and earlier papers);

I is formed by semihydrobenzoin transformation; II by vinyl dehydration or by semipinacolinic transformation; III by semipinacolinic transformation; and IV (or V) by oxidic dehydration.

The action of nitrous acid on the amino-alcohol derived from desylamine hydrochloride and magnesium α-naphthyl bromide is thus best interpreted on the basis of semipinacolinic deamination (compare McKenzie and Roger, *loc. cit.*), and we are inclined to adopt the view of the migrational aptitude of the phenyl group there advanced (p. 848, scheme A with $C_{10}H_7$ in place of Me).

On this basis, the compound described by McKenzie and Richardson is diphenylacetonaphthone (III). A change of this kind would be opposed to the view advanced by Elbs (*J. pr. Chem.*, 1887, [ii], **35**, 505) that the migrational aptitude of the naphthyl group is greater than that of the phenyl.

Through the kindness of Professor Tiffeneau we have just received a copy of his paper with M. Orékhoff (*Compt. rend.*, 1924, **178**, 1619) which was communicated to the French Académie des Sciences on May 12th. Those authors have isolated naphthyldeoxybenzoin (II) (which they found to melt at 108—109°) by the action of concentrated sulphuric acid on naphthylhydrobenzoin, and draw the conclusion that it is identical with the compound obtained by McKenzie and Richardson from β-hydroxy-αβ-diphenyl-β-naphthylethylamine. Their argument is based on the similarity of the melting points exhibited by those two distinct compounds.

We are at present continuing our study of the action of nitrous acid on compounds containing the group, $>\overset{|}{\underset{OH}{C}}—\overset{|}{\underset{NH_2}{C}}<$, with the object of extending our experience ultimately to optically active amino-alcohols.

## Experimental.

*Dehydration of α-Naphthylhydrobenzoin.*—The glycol (20 gms.) was boiled for 90 minutes with water (160 gms.) and concentrated sulphuric acid (200 gms.), the resulting viscous oil extracted with warm benzene, and the bulk of the benzene distilled off. The addition of ethyl alcohol caused the separation of diphenylnaphthylethylenic oxide (4 gms.), m. p. 180—181°. A determination of the molecular weight by the cryoscopic method showed that this oxide was unimolecular in benzene solution, whereas Mlle Lévy finds that the oxides formed by the dehydration of other glycols are usually bimolecular. The colourless solid (10 gms.), m. p. 101—109°, obtained from the mother-liquors was crystallised four times from benzene–ethyl alcohol, and the resulting product consisted of a mixture of large, transparent, rhombohedral prisms, and small

knots of amorphous solid. The prisms were picked out, and crystallised from benzene–ethyl alcohol.

*α-Naphthyldeoxybenzoin* (II), m. p. 109—110° (Found: C = 89·6; H = 5·7. $C_{24}H_{18}O$ requires C = 89·4; H = 5·6 per cent.), develops with cold concentrated sulphuric acid a reddish-brown coloration, changing in 5 minutes to a light yellow tint and, 10 minutes later, light green. The isomeride obtained by McKenzie and Richardson, m. p. 108—109° (the value originally quoted was 107—108°), and also by McKenzie and Roger developed a bright yellow tint at once, which did not change to a green.

From the action of concentrated sulphuric acid, either on naphthyl hydrobenzoin or on the ethylenic oxide, the isomeride, m. p. 108—109°, was isolated (McKenzie and Roger, *loc. cit.*). We have now found the isomeride, m. p. 109—110°, is also present in the low-melting solid mixture obtained from the mother-liquor from which the isomeride, m. p. 108—109°, was removed.

By repeated crystallisation of the solid which separated from the benzene mother-liquors after the dehydration of the glycol with dilute sulphuric acid, a mixture was obtained which melted at 104—106°. Six grams of the latter were boiled for 5 hours with a solution of 15 gms. of potassium hydroxide in a mixture of 90 c.c. of ethyl alcohol and 10 c.c. of water. On cooling, needles separated, and after recrystallisation from rectified spirit, 1·4 gms., melting at 152°, were obtained (Found: C = 93·7; H = 6·2. $C_{23}H_{18}$ requires C = 93·8; H = 6·2 per cent.). According to Ullmann and Mourawiew-Winigradoff, diphenylnaphthylmethane melts at 150° (*Ber.*, 1905, **38**, 2215). After the separation of this hydrocarbon the bulk of the alcohol was expelled, the residue poured into an excess of water, and extracted with ether. After removal of the ether, the yellow oil (3 gms.) was heated for 30 minutes with 3·5 gms. of picric acid dissolved in ethyl alcohol. On cooling, the picrate (m. p. 98—101°) was decomposed by aqueous potash, and the product extracted with ether. The resulting hydrocarbon was crystallised from alcohol, when 0·2 gm. of colourless, rectangular plates, m.p. 58°, was obtained (Found: C = 93·8; H = 6·4. $C_{17}H_{14}$ requires C = 93·6; H = 6·4 per cent.). According to Elbs (*J. pr. Chem.*, 1887, [ii], **35**, 465) phenylnaphthylmethane melts at 58·5°.

Benzoic acid (1·4 gms.) was isolated from the aqueous alkaline solution, and was identified by its m. p. 121—122° and by the analysis of its silver salt (Found: Ag = 46·9. Calc., Ag = 47·1 per cent.). The presence of formic acid was also detected.

*Constitution of the Isomeride, m. p.* 108—109°.

*Action of Alcoholic Potash.*—1·4 Grams of the compound, m. p. 108—109°, obtained by the dehydration of naphthylhydrobenzoin with concentrated sulphuric acid, was boiled for 6 hours with a solution of 2·5 gms. of potassium hydroxide in 25 c.c. of ethyl alcohol. The bulk of the alcohol was expelled, the residue poured into 100 c.c. of water, and extracted with ether. On expulsion of the ether an oil was obtained which on crystallisation from ethyl alcohol gave 0·7 gm. of the original ketone. The aqueous alkaline liquor was acidified by hydrochloric acid and extracted with ether. The resulting acid was crystallised from water, and 0·5 gm. separated. This was identified as α-naphthoic acid by its m. p. 159·5—160·5°, and by the analysis of its silver salt (Found : Ag = 38·7. Calc., Ag = 38·7 per cent.). This result indicates that the compound in question is diphenylacetonaphthone, which had undergone hydrolysis by the alkali : $\begin{matrix}CHPh_2\text{–}\\ H\text{–}\end{matrix}\!\!\begin{matrix}\text{–}CO\cdot C_{10}H_7.\\ \text{–}OH\end{matrix}$

*Oxidation.*—Two grams were oxidised by a solution of chromic anhydride (7 gms.) in glacial acetic acid (20 c.c.). The solution was poured into cold water, and the ethereal extract shaken with caustic soda. The alcoholic solution of the product was acted on by semicarbazide hydrochloride and sodium acetate. Plates of benzophenone semicarbazone separated, and the melting point of the semicarbazone prepared from an authentic specimen of benzophenone was not depressed when the two were mixed.

*Synthesis by the Action of Naphthalene and Aluminium Chloride on Diphenylacetyl Chloride.*—The acid chloride was prepared by the action of thionyl chloride on diphenylacetic acid. The Friedel and Crafts' action was carried out in the usual manner, carbon disulphide being used as the solvent. The naphthalene was subsequently removed from the resulting oil by distillation in steam. By crystallisation of the residue from ethyl alcohol, glistening, rhombic plates, m. p. 107—108°, were obtained.

*Synthesis by the Action of Magnesium α-Naphthyl Bromide on Diphenylacetyl Chloride.*—The addition of a Grignard reagent to an acid chloride cannot usually be regulated so that the action is restricted to the formation of a ketone, but Acree (*Ber.*, 1904, **37**, 628), for example, has shown that phenyl α-naphthyl ketone is formed by the interaction of magnesium α-naphthyl bromide and benzoyl chloride. We have found that diphenylacetyl chloride resembles benzoyl chloride in this unusual behaviour. Five grams of the acid chloride were added to the Grignard reagent prepared from 6 grams of α-bromonaphthalene, the usual procedure being

adopted. The product consisted of glistening, rhombic plates of diphenylacetonaphthone, m. p. 108—109° (Found: C = 89·3; H = 5·7. $C_{24}H_{18}O$ requires C = 89·4; H = 5·6 per cent.). Admixture with the compound, m. p. 108—109°, obtained by the dehydration of naphthylhydrobenzoin with concentrated sulphuric acid, showed no depression of the melting point.

One of us (W. S. D.) gratefully acknowledges the assistance rendered to him by a grant from the Department of Scientific and Industrial Research. We are also indebted to Dr. Robert Roger for his criticism.

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## CCLXXVII.—*The Colorimetric Dissociation Constants of the Mono- and Di-nitroquinols.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and GLENCOE RONALD NUNN.

DINITROQUINOL was prepared by Nietzki's method (*Annalen*, 1882, **215**, 143). Quinol diacetate (from 30 gms. of quinol) was nitrated in nitric acid (215 c.c.; *d* 1·5) below 10°, the mixture poured after 10—15 minutes into ice-water (2 litres), and the precipitate, after being partly dried, was hydrolysed by boiling dilute sulphuric acid (75 c.c. to each gram of precipitate); yield 30 per cent. The product melted at 134—136° and was shown to be 100 per cent. dinitroquinol by a method already described (Colver and Prideaux, *J. Soc. Chem. Ind.*, 1917, **36**, 480).

According to Kehrmann and Klopfenstein (*Helv. Chim. Acta*, 1923, **69**, 952), nitration of the quinol diacetate gives 3 : 5-dinitroquinol monoacetate. This corresponds with 2 : 6-dinitroquinol as stated by Bader (*Z. physikal. Chem.*, 1890, **6**, 289), who obtained his preparation from Nietzki, and not with 2 : 5-dinitroquinol as stated in Beilstein's "Organische Chemie." When treated with buffer solutions at various acidities, the compound developed colours agreeing with those described by Henderson and Forbes (*J. Amer. Chem. Soc.*, 1910, **32**, 687).

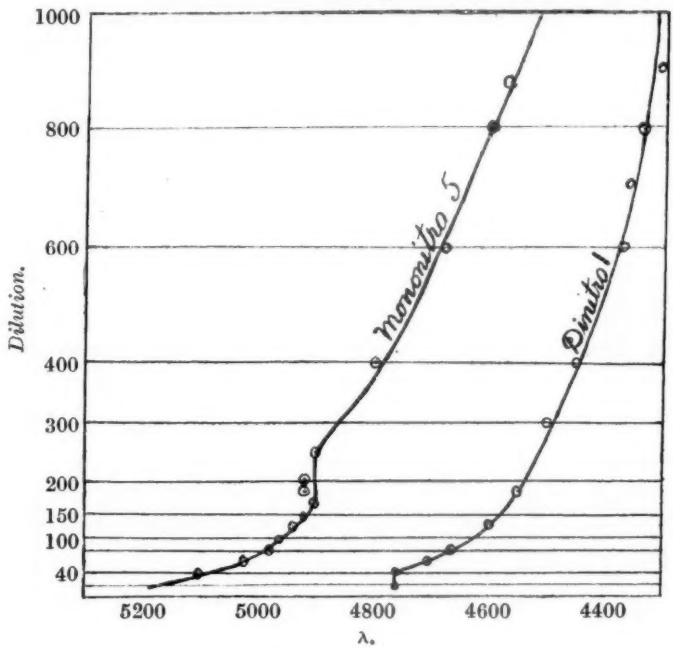
*Absorption Spectra.*—The solutions were prepared from a *M*/20-solution of dinitroquinol (0·5 gm. in 50 c.c. of alcohol) by suitable dilution. The *M*/20-solution gave complete absorption (observed with a spectroscope) from $\lambda = 0{\cdot}475\ \mu$ downwards. The limit of absorption moved towards the violet with increasing dilution and

no light was transmitted at the violet end of the visible spectrum. The absorption was of the ordinary nitrophenol type with no band in the visible spectrum (Fig. 1).

The absorption of a neutral (orange) solution was observed in a mixture of 40 c.c. of $M$/10-potassium dihydrogen phosphate and 60 c.c. of $M$/10-disodium hydrogen phosphate ($p_H = 6{\cdot}75$). When the $M$/20-dinitroquinol (5 drops) was mixed with varying quantities of the neutral buffer, a distinct absorption band was obtained,

FIG. 1.

*Dinitro- and mononitro-quinols in alcohol.*




a portion of the violet end of the spectrum being visible in the most concentrated solutions. As the amount of phosphate solution was increased from 3 to 9 c.c., the limits of absorption approached each other. The (violet) colour of an alkaline solution was examined as follows: 5 drops of the $M$/20-solution were added to 1 c.c. of 2$N$-sodium hydroxide, and diluted with 2, 3, and up to 9 c.c. of water. The curves of absorption are plotted in Fig. 2.

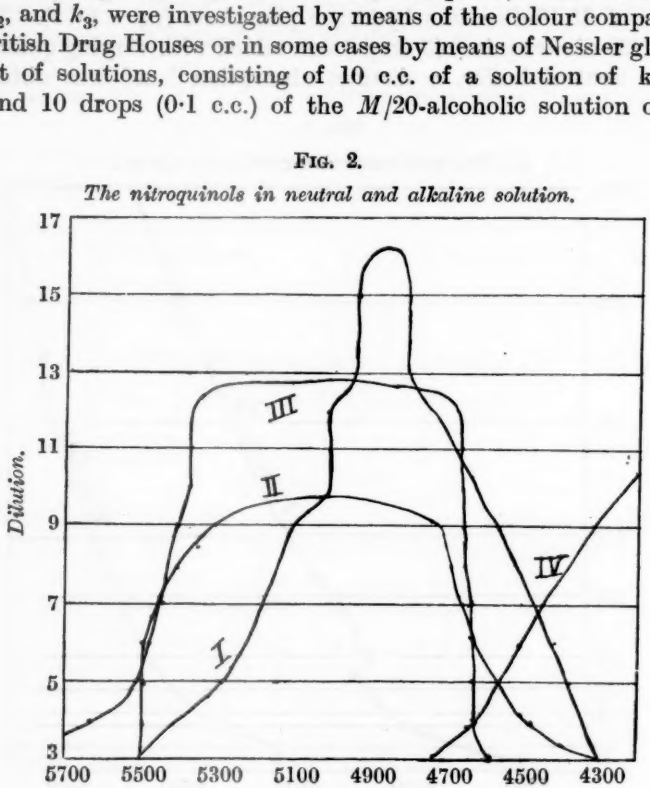
The absorption of the compound in acid solution was too weak to allow its examination by this simple visual means.

*Colorimetric Constants.*—The yellow, orange, and violet forms, which are distinct in their appearance and give distinct absorption

spectra, will, in their dependence on the $p_H$ of the buffer solutions, correspond to three colorimetric constants containing the tautomeric and electrometric constants according to the equations developed by Noyes and others (*J. Amer. Chem. Soc.*, 1910, **32**, 815; "Theory and Use of Indicators," Chap. IV). The constants, $k_1$, $k_2$, and $k_3$, were investigated by means of the colour comparator of British Drug Houses or in some cases by means of Nessler glasses. A set of solutions, consisting of 10 c.c. of a solution of known $p_H$ and 10 drops (0·1 c.c.) of the $M/20$-alcoholic solution of the

FIG. 2.

*The nitroquinols in neutral and alkaline solution.*




I. *D.N.Q. orange.* II. *D.N.Q. violet.* III. *M.N.Q. violet* IV. *M.N.Q. orange.*

indicator, and ranging from $p_H$ 2·0 to 7·5 in steps of 0·5, was sealed up in test-tubes of nearly equal bore. The first tinge of orange occurred at $p_H = 3·0$, was pronounced at $p_H = 3·5$, and deepened as $p_H$ increased. The first violet tint appeared at $p_H = 8·0$ and was fully developed at $p_H = 9·5$ to 10. The tube at $p_H = 2·5$ was the last which showed a pure yellow colour.

The fractions transformed at different values of $p_H$ were found by comparison with an alkaline solution of dinitrophenol which, it was assumed, would have at corresponding concentrations a yellow colour identical with that which would be shown by the dinitro-

quinol if it could be completely changed into the yellow form without any further change into the orange. The method of finding the degree of transformation by means of the completely transformed indicator has been used by Salm (*Z. physikal. Chem.*, 1906, **57**, 471) to determine the dissociation constants of indicators, and by Gillespie (*J. Amer. Chem. Soc.*, 1920, **42**, 242), Michaelis and Gyemant (*Biochem. Z.*, 1920, **109**, 165), and Kolthoff (*Z. Unters. Nahr. Genussm.*, 1921, **41**, 114) to determine the $p_H$ of a solution. If $x$ and $N - x$ are the numbers of drops of indicator in tubes 1 and 2 completely transformed in the one direction and the other—in this case 0·05$N$-dinitrophenol in alkaline and 0·2$N$-dinitroquinol in acid solution—and the combination exactly matches $N$ drops of partly transformed dinitroquinol in tube 3 of known $p_H = 2{\cdot}5$ (behind which is a tube of water), then $p_k = p_H + \log x/(N - x)$.

The measurements were made by dropping the $M/20$-solution of the indicator into the three tubes, keeping the number of drops in tube 3 equal to the sum of the drops in tubes 1 and 2.

| Tubes | | *1* | *2* | *3* |
|---|---|---|---|---|
| Drops | (*a*) | 2 | 6 | 8 |
| | (*b*) | 3 | 6 | 9 |
| | (*c*) | 3 | 7 | 10 |

The match was good in all these cases, and hence the values of $p_k$ are 2·98, 2·80, and 2·88 (mean 2·9). As a check on this experiment another was done in which five tubes were prepared as follows :

1. 10 c.c. of 0·2$N$-sodium hydroxide + 5 drops of $M/20$-dinitrophenol.
2. ,, of 0·2$N$-hydrochloric acid + 5 drops of $M/20$-dinitroquinol.
3. ,, of universal buffer solution of $p_H = 2{\cdot}8$.
4. ,, ,, ,, ,, $= 2{\cdot}9$.
5. ,, ,, ,, ,, $= 3{\cdot}0$.

Tubes 3, 4, 5, each containing 10 drops of $M/20$-dinitroquinol, were matched individually with 1 and 2 conjointly; tube 3 gave the best match, hence $p_k$ was taken as 2·8.

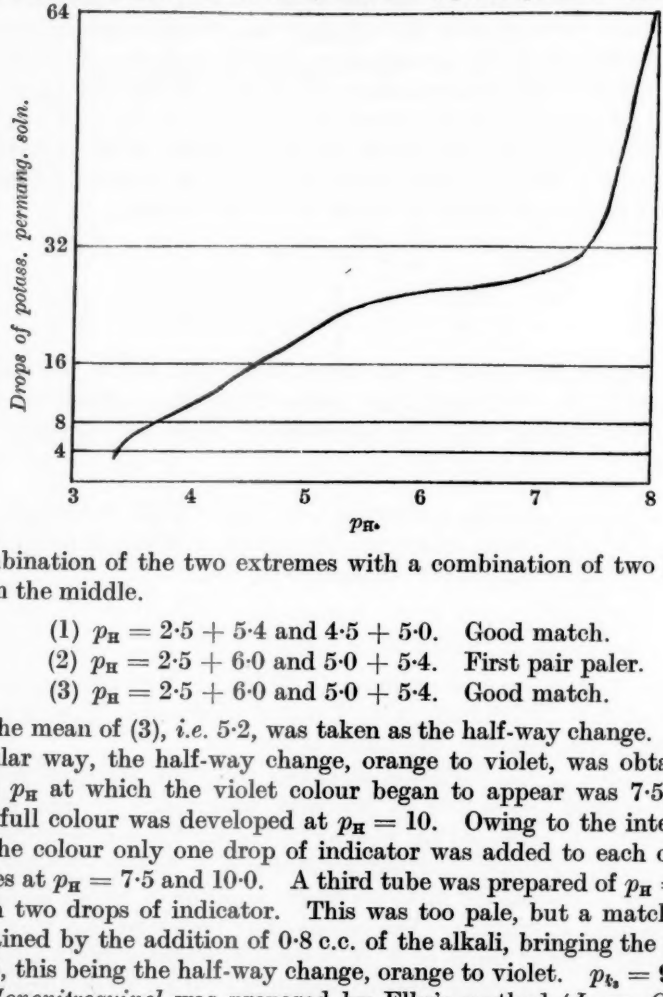
Some idea of the variation in colour from the first appearance of the orange ($p_H = 3{\cdot}0$) to the first appearance of the violet ($p_H = 8{\cdot}0$) was obtained by placing 25 c.c. of the universal buffer solution and 10 drops of indicator solution in a Nessler cylinder and gradually increasing the $p_H$ to 8·0 by the addition of known amounts 0·2$N$-sodium hydroxide. The colour thus produced was matched by the addition of drops of $N/10$-potassium permanganate solution to about 20 c.c. of water already containing 3·0 c.c. of $N/10$-potassium dichromate solution. The curve obtained by plotting $p_H$

against the number of drops of permanganate showed a big increase in the colour between $p_H = 7{\cdot}5$ and 8·0 (Fig. 3).

*The Second Constant.*—The orange colour, which was first evident at $p_H = 3{\cdot}0$, increased in intensity until $p_H = 5{\cdot}4$, from which point it remained constant, as far as the eye could judge, until $p_H = 7{\cdot}5$. Hence $p_H = 5{\cdot}4$ was taken as the point at which the full orange is developed. The half-way change was found by matching the

FIG. 3.

*$p_H$ of dinitroquinol and colour of dichromate, permanganate standards.*




combination of the two extremes with a combination of two tubes from the middle.

(1) $p_H = 2{\cdot}5 + 5{\cdot}4$ and $4{\cdot}5 + 5{\cdot}0$. Good match.
(2) $p_H = 2{\cdot}5 + 6{\cdot}0$ and $5{\cdot}0 + 5{\cdot}4$. First pair paler.
(3) $p_H = 2{\cdot}5 + 6{\cdot}0$ and $5{\cdot}0 + 5{\cdot}4$. Good match.

The mean of (3), *i.e.* 5·2, was taken as the half-way change. In a similar way, the half-way change, orange to violet, was obtained. The $p_H$ at which the violet colour began to appear was 7·5, and the full colour was developed at $p_H = 10$. Owing to the intensity of the colour only one drop of indicator was added to each of the tubes at $p_H = 7{\cdot}5$ and 10·0. A third tube was prepared of $p_H = 8{\cdot}0$ with two drops of indicator. This was too pale, but a match was obtained by the addition of 0·8 c.c. of the alkali, bringing the $p_H$ to 9·05, this being the half-way change, orange to violet. $p_{t_2} = 9{\cdot}05$.

*Mononitroquinol* was prepared by Elbs's method (*J. pr. Chem.*, 1893, [ii], **48**, 179). A mixture of *o*-nitrophenol (35 gms.), sodium

hydroxide (50 gms.), and ammonium persulphate (50 gms.) in water (1500 c.c.) was acidified after 48 hours, the excess of *o*-nitrophenol was removed with steam, and the mononitroquinol was extracted from the concentrated solution with chloroform.

The absorption spectra were examined in alcoholic, neutral, and alkaline solution exactly as in the case of the dinitro-compound. The curves are shown in Figs. 1 and 2.

*Colorimetric Constants.*—Standards of mononitroquinol in solutions of various $p_H$ were prepared in the same way as the dinitro-standards. The first constant was found by means of alkaline dinitrophenol and acid nitroquinol in the comparator, using a tube of $p_H = 3{\cdot}0$ as being the last point before any orange colour is developed. Three tubes were prepared as before and the good matches gave $p_k$ as 3·23 and 3·30. This was checked as in the former case by finding the buffer $p_H$ which matched the superimposed acid and alkaline nitroquinol. This $p_H$ was 3·22 and 3·30. The value of $p_{k_1}$ is 3·25.

*The Second and Third Constants.*—The first tinge of orange was shown at $p_H = 5{\cdot}5$ and the first tinge of violet at $p_H = 9{\cdot}5$, the intervening points showing a gradual increase in the depth of the orange tint. The half-way change was found as before to be at $p_H = 7{\cdot}6$ or 7·7. This was checked as before by finding a buffer solution which exactly agreed with the superimposed combination $p_H = 5{\cdot}5$ and 9·0. Thus $p_{k_2}$ is 7·6.

The half-way change, orange to violet, was found in the same way. The first trace of violet appears at $p_H = 9{\cdot}5$ and the full colour at $p_H = 11{\cdot}0$. A combination of these two matched very well with a combination $p_H = 10{\cdot}0$ and 10·5. The check experiment, *i.e.*, matching combinations $p_H = 9{\cdot}5$ and 11·0 each with 3 drops of indicator (owing to the intensity of the colour) against a tube of gradually increasing $p_H$, gave $p_{k_2} = 10{\cdot}2$.

*Comparison between the Colorimetric Constants of Nitroquinols and Nitrophenols.*—For reasons given in the literature, the colorimetric constant is not an exact measure of the strength of an acid. In the case of acids which consist of two tautomerides in equilibrium (the *pseudo-* and *aci*-forms) the electrometric constant, $k_e$ (*e.g.*, from conductivity), contains those of the two forms. The true constant of the *aci*-form cannot be obtained, but there is little doubt that it is the main factor controlling both $k_e$ and $k_c$. Also these two often run closely parallel, as is seen in the table.

There is some variation in the electrometric constants of the nitrophenols as given by Hantzsch, Bader, and others, but the means in each case are close to $1 \times 10^{-7}$. The colorimetric constant of *o*-nitrophenol is not very certain. Those of the *p*- and *m*-com-

pounds are well established by Michaelis and his co-workers (*loc. cit.*). The first constant of mononitroquinol should be compared with that of its nearest analogue, *o*-nitrophenol. The analogue of dinitrophenol, according to the view taken of its orientation, is either 2 : 6-dinitrophenol or 2 : 5-dinitrophenol. The nitrophenols should be weaker acids than the corresponding nitroquinols, and the table shows that this is the case.

The proportional increase is much less in the case of the dinitrocompound, and this is what we should expect, since the proportion present in the strong or *aci*-form at a given $p_H$ should depend on the number of ways in which the exchange of electrons giving the quinonoid form can take place, and this on the number of hydroxyl as well as of nitro-groups. The probabilities of such exchange are increased in a greater proportion when a hydroxyl group is added to a nitrophenol than when it is added to a dinitrophenol.

*Table of Constants.*

| Compound. | $k_c$. | $p_k$. | $k_c$. | $p_{k_1}$. | $p_{k_2}$. | $p_{k_3}$. |
|---|---|---|---|---|---|---|
| *o*-Nitrophenol | $1\times10^{-7}$ | 7 | $9\times10^{-7}$ | 6·05 | | |
| *p*- ,, | — | — | 6·3 to $9·2\times10^{-8}$ | 7·1 | | |
| *m*- ,, | — | — | 4·5 to $4·8\times10^{-9}$ | 8·33 | | |
| Mononitroquinol | — | — | $5·6\times10^{-4}$ | 3·25 | 7·2 | 10·2 |
| Dinitrophenol (2 : 6) | $1·74\times10^{-2}$ | 1·76 | 2 to $2·6\times10^{-4}$ | 3·65 | | |
| Dinitrophenol (2 : 5) | $7\times10^{-4}$ | 3·16 | $7\times10^{-6}$ | 5·15 | | |
| Dinitroquinol | $7·1\times10^{-9}$ | 2·15 | $1·6\times10^{-3}$ | 2·8 | 5·2 | 9·05 |

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# CCLXXVIII.—*Derivatives of* 1 : 8-*Naphthalic Acid. Part I. The Preparation and Properties of* 1 : 8-*Naphthalyl Chloride.*

By FREDERICK ALFRED MASON.

NAPHTHALIC anhydride (from 1 : 8-naphthalenedicarboxylic acid) differs very considerably from phthalic anhydride and its substitution products in the ease with which it condenses with other substances. A few derivatives of the phthalein type have been prepared from it, such as phenolnaphthalein (Jaubert, *Ber.*, 1893, **26**, 992) and the corresponding naphthafluorescein (Terrisse, *Annalen*, 1885, **227**, 135); the yields, however, are poor and the reactions far from smooth.

Attempts at replacing phthalic anhydride by naphthalic anhydride in the usual benzoyl-*o*-benzoic acid type of condensation having been unsuccessful, the anhydride being recovered almost quantitatively in nearly all cases, it was thought that the desired

1-benzoyl-8-naphthoic acid might be obtained by the use of naphthalyl chloride, if the latter could be prepared.

The desired acid chloride has been obtained by the prolonged action of a large excess of phosphorus pentachloride upon the anhydride in presence of phosphoryl chloride as a solvent, the yield being about 70% to 75%.

The *chloride*, $C_{10}H_6(COCl)_2$ or $C_{10}H_6\langle\begin{matrix}CO\\CCl_2\end{matrix}\rangle O$, forms large, colourless, transparent, rhombic crystals, m. p. about 84—86°. Unlike phthalyl chloride, it is immediately decomposed by water to form the anhydride, and cannot be preserved in an ordinary stoppered or corked bottle; even in a sealed tube the crystals rapidly lose their lustre. The crystals fume very strongly in the atmosphere until they have become coated with a protective layer of anhydride, which does not, however, prevent the inner layers from further gradual attack by atmospheric moisture. Attempts to distil the chloride under reduced pressure resulted in rapid and complete decomposition.

The chloride reacts vigorously with phenol to give phenolnaphthalein (Jaubert, *loc. cit.*), with resorcinol to give naphthafluorescein (Terrisse, *loc. cit.*), and with mono- and di-alkylated *m*-aminophenols to yield the corresponding *naphtharhodamines*, which possess crimson colours similar to those of the ordinary rhodamines, but have not so far been obtained in a pure form.

With alcohols naphthalyl chloride reacts to give mixtures of the normal di-esters and naphthalic anhydride; the diethyl ester, which is otherwise a difficult substance to obtain (Errera, *Gazzetta*, 1911, **41**, i, 190), can be prepared in very good yield.

Under carefully chosen conditions the chloride can be condensed with benzene by means of aluminium chloride to give the hitherto unknown 1 : 8-benzoylnaphthoic acid, the preparation of which is described elsewhere. The great reactivity of the chloride should make it a valuable reagent and condensations with its aid are now being investigated.

Since the chloride reacts immediately with aniline in dry ethereal solution to give a bright yellow product, it probably has the symmetrical structure (compare Ott, *Annalen*, 1912, **392**, 245). This would agree also with the fact already mentioned, that it reacts with benzene at low temperatures to give 1 : 8-benzoylnaphthoic acid (compare Copisarow, J., 1917, **111**, 10).

## Experimental.

A mixture of naphthalic anhydride (100 gms., recrystallised from hot 70% nitric acid [Jaubert, *loc. cit.*] and dried in the steam-oven),

phosphorus pentachloride (150 gms.; 1½ mols.), and phosphoryl chloride (150 c.c.) was heated under reflux uninterruptedly, and with exclusion of moisture, for 40—60 hours, the formation of lumps being prevented by occasional shaking during the first 24 hours. If the refluxing be interrupted at any time, the anhydride crystallises in lumps which need very prolonged boiling in order to redissolve them. The amber-coloured liquid obtained on cooling was filtered from a few crystals of unchanged anhydride through a well-dried Gooch crucible and distilled, preferably under reduced pressure. After 200 c.c. of phosphoryl chloride had been collected, the distillation was stopped, 150 c.c. of carefully dried carbon disulphide were added to the cooled product, and the whole was filtered into a well-dried flask. After standing several hours in ice, the naphthalyl chloride crystallised in colourless or pale yellow prisms; the mother-liquor was drained off from the crystals, the latter were washed with a few c.c. of solvent, and the residual solvent was removed by evacuating the flask.

The yield was about 61 gms.; from the mother-liquors after distilling off 100 c.c. of carbon disulphide and again standing in ice a further 25 gms. of the chloride were obtained but this fraction was not quite so pure and needed recrystallisation. Care must be taken at all stages of the preparation to prevent moist air from coming into contact with the preparation so far as possible. The total yield was therefore about 86 gms. or 68% (Found: Cl = 29·7. $C_{12}H_6O_2Cl_2$ requires Cl = 28·1%).

The chloride is easily soluble in phosphoryl chloride, chloroform, or tetrachloroethane, sparingly soluble in hot light petroleum (b. p. 100—120°). It is best recrystallised from carbon disulphide, in which it is easily soluble hot, but only sparingly soluble in the cold, crystallising when pure in large, well-formed, colourless, rhombic prisms.

*Action of the Chloride upon Alcohols.*—1. The diethyl ester. A solution of the acid chloride (10 gms. in dry chloroform, 50 c.c.) and absolute alcohol (50 c.c.) became warm on mixing and naphthalic anhydride (1·3 gms.) separated. The filtered solution was evaporated on the water-bath, the residual oil stirred with ice, and the solid (6·5 gms. after drying) recrystallised from dilute methyl alcohol; m. p. 58—60°.

2. The dimethyl ester was prepared in a similar manner; 3·8 gms. of anhydride were obtained, and 3·9 gms. of the ester, m. p. 101—102° after recrystallisation.

3. *Di*-n-*butyl ester*. Very little anhydride was formed. The ester (8·5 gms. from 10 gms. of chloride) was recrystallised from dilute methyl alcohol; m. p. 52—53° (Found: C = 73·7; H = 7·3. $C_{20}H_{24}O_4$ requires C = 73·2; H = 7·3%).

Attempts to prepare the dibenzyl ester in a similar manner gave a nearly quantitative yield of naphthalic anhydride, no ester being isolated.

The author's thanks are due to the British Dyestuffs Corporation for permission to publish the results, and to Prof. W. H. Perkin, F.R.S., for the interest he has taken in the work.

DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 11th*, 1924.]

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## CCLXXIX.—*Derivatives of* 1 : 8-*Naphthalic Acid. Part II. The Preparation and Properties of* 1-*Benzoylnaphthalene*-8-*carboxylic Acid and its Derivatives.*

By FREDERICK ALFRED MASON.

In view of the close analogy between the behaviour of phthalic anhydride, and 1 : 8-naphthalic anhydride (I), it seemed to be of interest to attempt the preparation of 1-benzoylnaphthalene-8-carboxylic acid (II) (referred to shortly as benzoylnaphthoic acid) by condensing naphthalic anhydride with benzene in presence of aluminium chloride, in the same way that benzoyl-*o*-benzoic acid may be prepared from phthalic anhydride and benzene by the usual Friedel-Crafts reaction :—

$$C_{10}H_6\!<\!\begin{matrix}CO\\CO\end{matrix}\!>O + C_6H_6 \longrightarrow \underset{\text{(I.)}}{C_{10}H_6\!<\!\begin{matrix}CO_2H\\COPh\end{matrix}} \longrightarrow \underset{\text{(II.)}}{} C_{10}H_6\!<\!\begin{matrix}CO\\CO\end{matrix}\!>C_6H_4 \quad \text{(III.)}$$

It was further hoped that from benzoylnaphthoic acid the diketone (III) might be formed by ring closure in a manner similar to the preparation of anthraquinone from benzoyl-*o*-benzoic acid.

Condensation between naphthalic anhydride and benzene was attempted, using varying amounts of aluminium chloride, benzene, and anhydride, with and without solvents such as carbon disulphide, tetrachlorethane, and nitrobenzene, at temperatures varying from 0° to the b. p. of nitrobenzene, but in almost all cases the anhydride was recovered nearly quantitatively. This is the more remarkable in that aluminium chloride reacted with the anhydride in presence of a solvent, such as nitrobenzene, to form a dark oily product, which did not, however, combine with the benzene and yielded the anhydride back again almost quantitatively on working up. The desired acid was ultimately prepared in good yield (average about 64%) from 1 : 8-naphthalyl chloride (preceding paper) by a modification of the method used by Copisarow (J., 1917, **111**, 10) for preparing benzoylbenzoic acid.

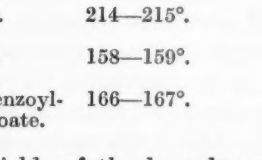
1-*Benzoylnaphthalene*-8-*carboxylic acid* (1 : 8-*Benzoylnaphthoic acid*) begins to decompose at its m. p., 110—112°; a vigorous bubbling takes place at 115—120°, presumably due to loss of carbon dioxide, leaving a residue of phenyl naphthyl ketone, but this has not yet been confirmed. In this respect benzoylnaphthoic acid differs markedly from benzoylbenzoic acid, which is quite stable at its melting point. Benzoylnaphthoic acid decomposes even at 100° on heating for a short time.

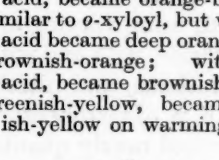
On heating the yellow to yellowish-brown solution of the acid in concentrated sulphuric acid on the water-bath no sign of ring closure could be detected, the acid being recovered unchanged on dilution, whereas benzoylbenzoic acid under such conditions gives a nearly quantitative yield of anthraquinone. The use of 5% oleum or phosphoryl chloride also failed to give the desired result, as also did phosphoric oxide in tetrachloroethane. Attempts to close the ring by treating the acid chloride with aluminium chloride in carbon disulphide solution have so far given negative results, the product being a viscous, reddish-brown gum which decomposed on heating. Further experiments are being carried out.

Using the same general method for the preparation of benzoylnaphthoic acid, the corresponding derivatives were prepared from toluene and from the three isomeric xylenes; the general properties are given in the following table :—

| Radical. | M. p. | Colour in conc. sulphuric acid. |
|---|---|---|
| Benzoyl. | 110—112° with slow decomp., rapid at 115°. | Clear, deep yellow to yellowish-brown. |
| Toluoyl. | 135—137°, then resolidified. | Orange; on adding a drop of nitric acid, became orange with green fluorescence. |
| *o*-Xyloyl. | 147—149°. | Brownish-scarlet, pink in thin layers. With a drop of nitric acid, became orange-brown. |
| *m*-Xyloyl. | 214—215°. | Similar to *o*-xyloyl, but with nitric acid became deep orange-yellow. |
| *p*-Xyloyl. | 158—159°. | Brownish-orange; with nitric acid, became brownish-yellow. |
| Ethyl benzoylnaphthoate. | 166—167°. | Greenish-yellow, became brownish-yellow on warming. |

The yields of the homologous acids were mostly poor. In the course of preparing the toluoylnaphthoic acid a substance, $C_{26}H_{20}O_2$, was obtained which must be either *ditolylnaphthalide* (IV) or 1 : 8-*ditoluoylnaphthalene* (V) :

(IV.) 

(V.)

So far this point has not been definitely decided, although from analogy with Copisarow's results formula (IV) appears the more likely. Attempts have been made to prepare the corresponding derivative from benzene but without success, the only products isolated being benzoylnaphthoic acid and a reddish-brown gum.

## EXPERIMENTAL.

1-*Benzoylnaphthalene*-8-*carboxylic Acid* (*Benzoylnaphthoic Acid* (Formula II).—To a mixture of dry benzene (8·4 c.c.) and tetrachloroethane (100 c.c.), well-powdered aluminium chloride (30 gms.) was added during 5 minutes. After remaining at room temperature for 2—3 hours with occasional shaking, the mixture was cooled in a freezing mixture and added, during 5—10 minutes, to a solution of 1:8-naphthalyl chloride (20 gms.) in tetrachloroethane (100 c.c.), similarly cooled. The mixture was kept in ice during the day, at room temperature for 24 hours, and at 30—40° for 1 hour. The thick brownish-black mixture was poured on to ice, and kept well stirred, the colour changing slowly from brown to green and finally to yellow, and the whole was then filtered. The tetrachloroethane was washed, and the free benzoylnaphthoic acid extracted from it by shaking twice with half-saturated sodium carbonate solution. The extract was shaken with charcoal, filtered, cooled to 0—5°, and acidified with 10—20% acetic acid. After 12 hours, the pasty mixture was filtered, and the precipitate washed well, purified by dissolution in lukewarm saturated sodium bicarbonate solution, and reprecipitated with acetic acid. After drying at 50—60°, the acid formed a pale cream-coloured powder (yield 14·4 gms., or 72%).

Variations in the amount of aluminium chloride did not appear to have any great influence on the yield. The acid may be recrystallised with care from 70% acetic acid, forming minute white needles, or from ether. It is very easily soluble in most other organic solvents (Found: C = 77·4; H = 4·6. $C_{18}H_{12}O_3$ requires C = 78·3; H = 4·3%).

1:8-*Benzoylnaphthoyl Chloride*, $COPh{\cdot}C_{10}H_6{\cdot}COCl$.—Crude benzoylnaphthoic acid (5·5 gms.) and thionyl chloride (4 c.c.) were heated on the water-bath for ½ hour after the initial vigorous reaction had subsided, 25 c.c. of hot benzene followed by 80 c.c. of petroleum (b. p. 60—80°) were added, a certain amount of red gum being deposited; well-dried charcoal was then added and the hot liquid filtered. On standing, nearly colourless, strongly refracting, rhombic crystals of the acid chloride separated, m. p. 125—127° (Found: Cl = 11·3. $C_{18}H_{11}O_2Cl$ requires Cl = 12·0%).

The chloride fumes slightly in the air and is slowly hydrolysed

by atmospheric moisture. Attempts have been made to effect ring closing by cautious treatment with aluminium chloride, but so far without success. Treatment of the chloride with absolute alcohol gave the *ethyl* ester, white prisms, m. p. 166—167°, easily soluble in hot benzene, moderately soluble in hot alcohol (Found: C = 78·3; H = 5·2. $C_{20}H_{16}O$ requires C = 78·7; H = 5·3%).

1-*Toluoylnaphthalene*-8-*carboxylic acid* (*toluoylnaphthoic acid*, $C_7H_7{\cdot}CO{\cdot}C_{10}H_6{\cdot}CO_2H$), was prepared in a similar manner to the benzoylnaphthoic acid, using naphthalyl chloride (10 gms.), toluene (4 c.c.), aluminium chloride (15 gms.) and tetrachloroethane (50 c.c.). Product 2·7 gms. After recrystallising from 70% acetic acid, it formed white needles, m. p. 175—177° (heated slowly); in a bath at 150° the acid melted and then quickly resolidified, whilst if first placed in a bath at 125° it melted fairly sharply at 135—137° (Found: C = 78·5; H = 5·2. $C_{19}H_{14}O_3$ requires C = 78·6; H = 4·8%).

*Ditolylnaphthalide* 1:8, (?) *or* 1:8-*Ditoluoylnaphthalene* (?) (IV or V).—Crushed aluminium chloride (50 gms.) was added by degrees, with ice cooling, to a mixture of crude 1:8-naphthalyl chloride (60 gms.) and purified toluene (400 c.c.), and, after 4 hours, the deep purplish-brown liquid was heated to 40°; next day, the temperature was raised slowly to 80° and finally the mixture was heated on the water-bath. After cooling, it was decomposed with ice and dilute hydrochloric acid, becoming pale brown and pasty. The solid (40 gms. after pressing and drying) crystallised from glacial acetic acid in colourless, glistening needles, m. p. 234°, which were insoluble in hot alcohol and dissolved in strong sulphuric acid to a deep scarlet-red solution (Found: C = 85·4; H = 5·5. $C_{26}H_{20}O_2$ rquires C = 85·7; H = 5·5%).

1:8-*Xyloylnaphthalenecarboxylic Acids*, $C_6H_3Me_2{\cdot}CO{\cdot}C_{10}H_6{\cdot}CO_2H$.—The condensation of the three xylenes with naphthalyl chloride followed the general method, and similar results were obtained except that the yields were much smaller than in the case of benzoylnaphthoic acid; the yields given in each case are from 10 gms. of the acid chloride. The three acids crystallise from 70% acetic acid in white needles: o-*xyloylnaphthoic acid* (yield 2·5 gms.), m. p. 147—149° (Found: C = 78·9; H = 5·2. $C_{20}H_{16}O_3$ requires C = 78·7; H = 5·3%); *m*-xyloylnaphthoic acid (yield 2·0 gms.), m. p. 214—215° (Found: C = 78·8; H = 5·4%); *p*-xyloylnaphthoic acid (yield 0·8 gms.), m. p. 158—159° (Found: C = 79·5; H = 5·2%).

*Summary.*

1-Benzoylnaphthalene-8-carboxylic acid has been prepared by condensing 1:8-naphthalyl chloride with benzene in presence of

aluminium chloride, in 64% yield, as a crystalline substance melting at 110—112°, and decomposing a few degrees above this temperature. The corresponding toluoyl-, *o*-, *m*- and *p*-xyloyl derivatives have been prepared and also a crystalline substance which is presumably ditolylnaphthalide.

The author's thanks are due to Prof. W. H. Perkin, F.R.S., and to the British Dyestuffs Corporation, Ltd., for permission to publish the results.

DYSON PERRINS LABORATORY,
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## CCLXXX.—*Studies in Fluorescence Spectra. Part III. Aromatic Amine Vapours.*

By THOMAS HENRY NUNAN and JOSEPH KENNETH MARSH.

UNTIL recently, it was not known in the case of substances ordinarily considered fluorescent, *i.e.*, exhibiting the phenomenon in dilute solutions, whether fluorescence was excitable in the vapour state, Dickson's negative result for benzene (*Z. wiss. Phot.*, 1910, **8**, 287) and Elston's positive result for anthracene (*Astrophysical J.*, 1907, **25**, 155), being at variance. The facts recorded in the former papers of this series (J., 1923, **123**, 3315; this vol., p. 418) leave no doubt that vapour fluorescence is commonly exhibited by substances possessing fluorescent powers in solution. Whilst at equal concentrations the emission of the solution is distinctly stronger than that of the vapour, yet the vapour spectrum has in many cases an added interest, for it often shows a number of fine bands not found in solution.

Among fluorescent substances, the aromatic amines are a conspicuous group characterised by considerable intensity, and in view of the resolution which has been obtained by examination of other fluorescence spectra in the vapour state it has seemed desirable to study the spectra of this class also as vapours and to make comparison with the previous observations of Ley and Englehardt (*Z. physikal. Chem.*, 1910, **74**, 1) or of Stark and Steubing (*Physikal. Z.*, 1908, **9**, 481). On the whole, the results of these observers have been fully confirmed, and the number of cases where any signs of resolution of the single broad fluorescent band into a finer structure has been observed has been disappointingly small. This may be due in part to experimental conditions. Thus many of the substances are not volatile at low temperatures, and at higher temperatures as sharp definition is not obtainable. Another adverse

circumstance was the high resolving power of the spectroscope which was available for use. An instrument with about three times the dispersion of the spectrograph used previously was employed in most of the present work, with the result that the spectra obtainable with an exposure of about three hours were very faint, and the finer bands were so dispersed as to render their detection difficult or impossible. It was customary to intensify the plates with mercuric chloride.

The other experimental arrangements remained substantially as previously described, but to render the manipulation of less volatile substances possible a silica tap funnel was fused on to the inlet tube of the observation cell and substances solid at the ordinary temperature could be dealt with fairly satisfactorily by heating the funnel and tap by resistance wire. A receiver with side tube for evacuating was also fused directly on to the other half of the cell. With the Littrow spectrograph used, only a portion of the spectrum could be photographed at a time. The usual portion examined lay between λλ 2910 and 5000, and there seems to be little probability of any fluorescence spectrum having escaped detection through falling entirely outside these limits, as absorption in the case of the aromatic amines usually reaches down from the more extreme ultra-violet to beyond 3000 Å.U. The ordinary fluorescence lay on the long wave-length side of the absorption, but finished at or before 5000 Å.U. and it is unusual for there to be more than one region of fluorescence.

In Table I are given details of the experimental conditions and results obtained and in Fig. 1 an attempt has been made to indicate the intensity of the fluorescence graphically.

Some of the substances call for individual comment.

*Aniline.* With the large spectrograph this substance showed little banding, but with the Hilger instrument used in previous work several bands were apparent at the end of shorter wave-length. The spectrum is more intense and more removed from the benzene region than that found in the case of other mono-substitution products so far examined. The bands measured were located as follows :—

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1/λ | 3408 | 3394 | 3367 | 3349 | 3338 | 3328 | 3263 | 3242 | 3210 | 3165 |
| | | 3392 | 3365 | | | | | | | |

*Alkyl anilines.* These showed some variations, although without apparent regularity. Most gave heavy films on the window of the cell under the action of light, but in the case of diethylaniline this film was less evident, and it seems not unlikely that the apparent strength and extent of the fluorescence are consequences.

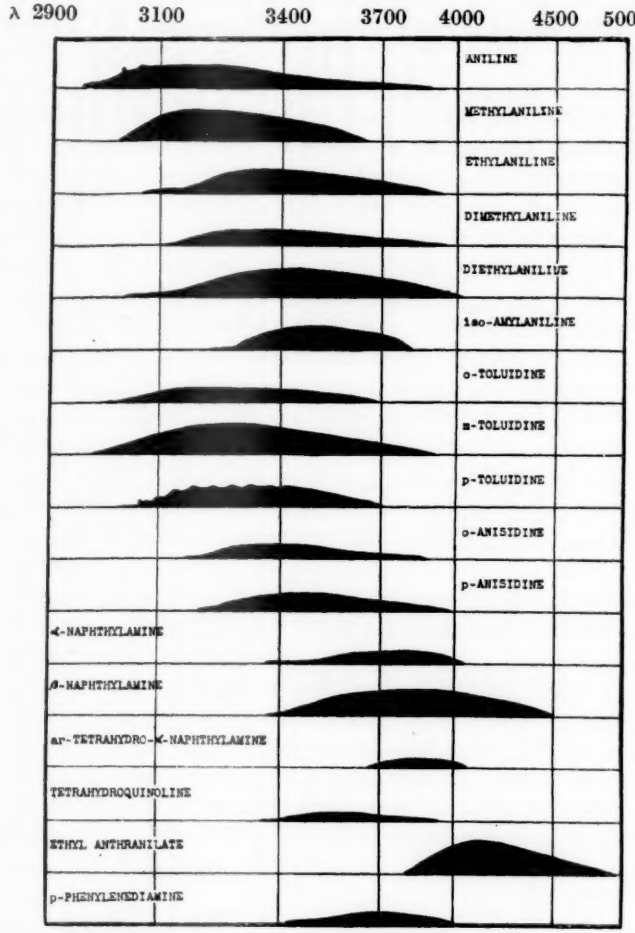
TABLE I.

| No. | Substance. | Fluorescence (1/λ). | Cell temp. | Pressure (mm.). | B. p. | M. p. | Remarks. |
|---|---|---|---|---|---|---|---|
| 1 | Aniline. | 3380—2560 | 100—110° | 11 | 183° | | Strong. Bands. Heavy film. |
| 2 | Monomethylaniline. | 3310—2755 | 120—130 | 11 | 194·8 | | Strong. Fairly heavy film. |
| 3 | Monoethylaniline. | 3185—2520 | 120—130 | 11 | 205 | | Strong. Moderate film. |
| 4 | Dimethylaniline. | 3225—2515 | 130 | 15 | 192·8 | | Strong. |
| 5 | Diethylaniline. | 3310—2480 | 130—140 | 11 | 215/759 | | Strong and extensive. Little film or decomposition. |
| 6 | *iso*Amylaniline. | 3080—2740 | 160 | 17 | 254/755 | | Short zone. Heavy brown film. |
| 7 | Benzylamine. | — | 130 | 18 | 184 | | |
| 8 | *o*-Toluidine. | 3355—2670 | 140 | 15 | 199/763 | | Much decomposition and film. |
| 9 | *m*-Toluidine. | 3390—2540 | 150 | 15 | 202·8 | | Very strong. Thick film. |
| 10 | *p*-Toluidine. | 3269—2720 | 150 | 15 | 200 | 43° | Regular banding. |
| 11 | *o*-Anisidine. | 3175—2565 | 150 | 17 | 224/766 | | Sudden change of intensity at about λ 3250. |
| 12 | *p*-Anisidine. | 3145—2540 | 140 | 10 | 243 | 57·6 | Very heavy film. |
| 13 | α-Naphthylamine. | 2940—2470 | 200 | 11 | 300 | 50 | Faint. Strong film. |
| 14 | β-Naphthylamine. | 2960—2220 | 180 | 10 | 294 | 111 | Medium. Very slight film. |
| 15 | *ar*-Tetrahydro-α-naphthylamine. | 2705—2475 | 190—200 | 10 | 275/712 | | Faint. Little film. |
| 16 | *ac*-Tetrahydro-β-naphthylamine. | — | 150—160 | 10 | 240·5 | | Decomposition and heavy film. |
| 17 | Tetrahydroquinoline. | 2990—2520 | 150—160 | 11 | 247 | | Very faint. |
| 18 | Ethyl anthranilate. | 2645—2000 | 160—170 | 11 | 266/770 | | Intense though very heavy film. |
| 19 | Diphenylamine. | — | 190 | 9 | 310 | 54 | Fluorescent only in solution. |
| 20 | *p*-Phenylenediamine. | 2520—2035 | 170 | 9 | 267 | 140 | Faint. Considerable decomposition. |

*Benzylamine.* Three plates were taken, but in no case was any fluorescence observed.

*Toluidines.* The fluorescence of *m*-toluidine was particularly strong and *p*-toluidine gave the most banded spectrum among

FIG. 1.




substances here dealt with. Bands were observed with the smaller spectrograph as under :—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1/λ | 3327 | 3267 | 3226 | 3183 | 3143 | 3099 | | | |
| | | 3263 ? | 3220 | | 3136 | 3092 | 3051 | 3008 | 2966 |

There is a high degree of regularity among them, the interval being about 42 units. Of disubstituted benzene derivatives, it has always

been found that para-substitution is accompanied by the most distinct fine banding, this being often equal to or greater than the banding in mono-substituted compounds. *p*-Cresol (this vol., p. 418) and *p*-xylene (p. 1743) also give spectra characterised by bands at regular intervals of about 40 units. These three substances all have para groups of approximately equal weights. In *p*-tolyl methyl ether, where one group is much heavier than the other, this same banding is not found. Neither is it seen in *p*-anisidine or *p*-phenylenediamine. It is hoped to treat of the whole subject of banding in a separate paper shortly, and the subject need not be pursued further at this juncture.

p-*Phenylenediamine* proved rather unstable under the influence of light and heat. A heavy film was formed, possibly accounting for the faint spectrum obtained.

ar-*Tetrahydro-α- and* ac-*tetrahydro-β-naphthylamines* maintained their usual aromatic and aliphatic characteristics respectively in regard to their fluorescence. The latter, which has the amino-group attached to a fully saturated ring, behaves like the simple aliphatic amines in giving no fluorescence. The former, which has the amino-group attached to a benzenoid ring, shows fluorescence.

*Tetrahydroquinoline* gave a faint fluorescence.

*Diphenylamine* could not be observed to fluoresce. This substance has the highest boiling point of any examined. Nevertheless it does not appear possible that it failed to vaporise, but seemingly the high temperature has destroyed its fluorescent properties. The fact that it is fluorescent in solution was confirmed. The fluorescence was still well marked at *M*/2000, which concentration was of the same order as that of the vapour examined. Other substances of high boiling points also gave weaker spectra than might have been expected. Thus one would anticipate that the naphthylamines, and also *p*-phenylenediamine, would have strong spectra, but such was not found to be the case.

With *ethyl anthranilate*, the introduction of an ester group is seen to have produced a large shift of the fluorescence towards longer wave-lengths. A just similar effect was previously observed in the case of methyl salicylate. Most of the amines, however, fluoresce in much the same region and with the greatest intensity between about λλ 3100 and 3500.

On comparing the vapour spectra with the measurements made by Ley and Englehardt and Stark it is seen that there is the usual shift towards the end of greater wave-length in solution, but a considerable increase in intensity. Benzylamine, which in solution gives a weak fluorescence, could not be observed to give any from the vapour. In the case of *o*-anisidine and tetrahydroquinoline

the solution spectrum recorded is more extensive at both ends. With monoethylaniline and dimethylaniline the vapour spectra are the more extensive.

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# CCLXXXI.—*The Chemistry of the Glutaconic Acids. Part XVII. The Tendency towards Reversion to Type.*

By CHRISTOPHER KELK INGOLD, JAMES HERBERT OLIVER, and JOCELYN FIELD THORPE.

MANY observations have been made which show the remarkable tendency of the mobile glutaconic system towards survival. Thus if the mobile system is destroyed, the chief characteristic of the substances so formed is their tendency to revert to compounds of the original mobile type. These "reversions to type" show, moreover, a certain family resemblance, and this phenomenon is one of the several outstanding features of glutaconic chemistry which the conventional theory of Feist ignores. Three examples may be given.

(1) When a mobile glutaconic ester of type (I) is alkylated, the mobile hydrogen atom becomes replaced and the tautomeric system becomes blocked. The product (II) exhibits notable instability, passing back into an ester (III) of the mobile series in presence of a trace of cold sodium ethoxide in alcohol, the obstructing carbethoxyl group being expelled as ethyl carbonate:

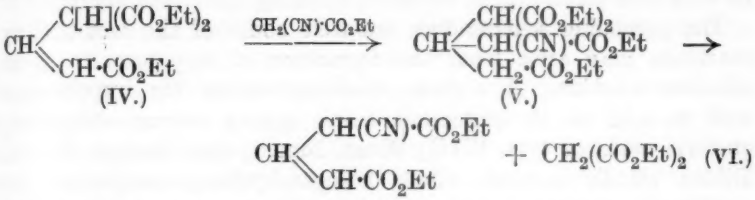
$$\underset{\text{(mobile; stable to NaOEt)}}{(CO_2Et)_2C[H]\cdot CH{:}C(CO_2Et)_2\ (I.)} \xrightarrow{\text{(alkylation)}} \underset{\text{(static; unstable to NaOEt)}}{(CO_2Et)_2CR\cdot CH{:}C(CO_2Et)_2\ (II.)}$$

$$\xrightarrow[\text{of NaOEt}]{\text{trace}} \underset{\text{(mobile; stable to NaOEt)}}{CO_2Et\cdot CR[H]\cdot CH{:}C(CO_2Et)_2\ (III.)} + EtO\cdot CO_2Et$$

(Thole and Thorpe, J., 1911, **99**, 2187; compare also Ingold and Thorpe, J., 1919, **115**, 143).

(2) The mobile (normal) glutaconic esters, as a class, strongly resist the destruction of their tautomeric three-carbon system by the addition of substances of the type of ethyl malonate and ethyl cyanoacetate (Thorpe and Wood, J., 1913, **105**, 1579; Thorpe, J., 1919, **115**, 679; Ingold, J., 1921, **119**, 341). In certain cases (IV, for example) the addition (Michael) reaction does take place, but the derivatives of methanetriacetic acid so formed (V) are exceedingly unstable, and break down (retrograde Michael reaction),

often spontaneously, to give new esters of the mobile glutaconic type (VI):



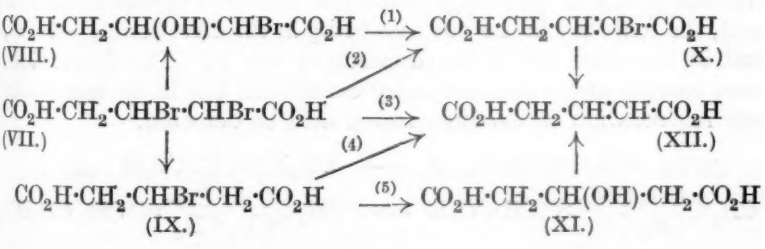
(Ingold and Perren, J., 1921, **119**, 1582; 1922, **121**, 1414; Ingold, J., 1922, **121**, 1147).

(3) When glutaconic acid is treated with bromine, a static dibromo-additive product is obtained, which on treatment with alkalis passes back into glutaconic acid, reduction accompanying the hydrolytic action of the alkali, although no reducing agent is present (Farmer and Ingold, J., 1921, **119**, 2001). This fact, and a similar one relating to a bromine compound in the *cyclo*propane series (Goss, Ingold, and Thorpe, J., 1923, **123**, 327), although they obviously represent a third general reaction by which reversion to type is attained, have hitherto remained isolated observations in glutaconic chemistry, and therefore it was decided to carry out a general investigation of this reaction in order to place it on the same broad experimental basis as the reactions in sections (1) and (2) above.

Our attention has been focussed mainly upon two points, (*a*) the mechanism of the reaction, (*b*) the facility with which it occurs in relation to the mobility of the structures produced.

### (a) *Mechanism of the Reaction.*

Five possibilities suggest themselves, which are illustrated by the following formulæ:



Although none of these possibilities can be dismissed *a priori*, reasons can be given for regarding all of them as improbable excepting (2). The isolation of intermediate compounds of type (X) and their ready conversion into those of type (XII) clearly

indicate mechanism (2) as the correct one; nevertheless, the possible modification represented by mechanism (1) cannot definitely be excluded when alkalis are used to bring about the change.

The preceding scheme does not take count of the fact that by-reactions may arise from the formation of hypobromite in the alkaline solution. A certain tendency exists for hypobromous acid to add on to glutaconic acids, giving α-bromo-β-hydroxyglutaric acids of type (VIII) (Goss, Ingold, and Thorpe, *loc. cit.*). Dilute alkalis convert these halogen-hydroxy-compounds into αβ-dihydroxyglutaric acids, which are therefore very frequently formed as by-products in the reactions under discussion. The experiments now described render it almost certain that the production of αβ-dihydroxyglutaric acid,

$$CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CO_2H \text{ (XIII.)},$$

observed by Farmer and Ingold (*loc. cit.*), is to be traced to this cause.

(b) *Dependence of Reduction on Mobility.*

Glutaconic acids may be regarded both as αβ-unsaturated acids and as βγ-unsaturated acids, and in endeavouring to trace the relationship between the reduction-reaction and the mobility of the product it was necessary at the outset to ascertain whether the reaction was peculiar to glutaconic acids, and similar mobile series, or whether it was also displayed by static unsaturated acids, either of the αβ- or of the βγ-type. To test this point, two pairs of isomeric αβ- and βγ-unsaturated acids were selected, which were known to be static under the conditions employed to regenerate them from the dibromides, although interconversion might occur under other conditions (compare Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080). These acids were crotonic acid, vinylacetic acid, *cyclo*hexylideneacetic acid, and *cyclo*hexeneacetic acid (XIV, XV, XVI, and XVII). Vinylacetic acid can be converted into crotonic acid and *cyclo*hexylideneacetic acid into *cyclo*hexeneacetic acid, the tendency in the one case being in the direction βγ → αβ, and in the other case in the direction αβ → βγ. The dibromides were treated under the customary conditions, but in no case could any regeneration of the unsaturated acid be detected.

(XIV.) $CH_3{\cdot}CH{:}CH{\cdot}CO_2H \leftarrow CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$ (XV.)

$$CH_2\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!C{:}CH{\cdot}CO_2H \rightarrow CH_2\!<\!\begin{matrix}CH_2-CH\\CH_2{\cdot}CH_2\end{matrix}\!>\!C{\cdot}CH_2{\cdot}CO_2H$$

(XVI.) (XVII.)

On turning to the glutaconic acids themselves, a remarkable parallelism is observed between the tendency of the dibromides to regenerate the parent acids and the mobility of the acids thus

produced. Glutaconic acid itself is the most mobile of the series; the acid can be isolated in only one form, and the labile form of the ester has but a transitory existence. The introduction of substituents in either the α- or the β-position decreases the mobility. When one substituent is present the labile form of the acid can be isolated and the esters become only slowly interconvertible, whilst when two are present the characteristics of static geometrical isomerides may appear. Glutaconic acid dibromide is reduced with remarkable ease. The introduction of a single substituent of either electrical character, in either the α- or the β-position, appears insufficient to suppress the reaction; but two substituents, whether in the αβ- or αγ-positions, are effective in suppressing it. The following table shows the results of the experiments which have been carried out up to the present time:

| | | |
|---|---|---|
| Glutaconic acid. | $CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$ (XII). | Regenerated. |
| α-Methylglutaconic acid. | $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2H$ (XVIII). | ,, |
| β-Methylglutaconic acid. | $CO_2H{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H$ (XIX). | ,, |
| Aconitic ester. | $CO_2Et{\cdot}CH_2{\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et$ (XX). | ,, |
| αβ-Dimethylglutaconic acid. | $CO_2H{\cdot}CHMe{\cdot}CMe{:}CH{\cdot}CO_2H$ (XXI). | Not regenerated. |
| αγ-Dimethylglutaconic acid. | $CO_2H{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CO_2H$ (XXII). | ,, ,, |

Ruhemann and Allhusen state that the dibromide (XXIII) of ethyl aconitate yields a mixture of oxalic and succinic acids on hydrolysis with barium hydroxide (J., 1894, **65**, 10):

$$CO_2Et{\cdot}CH_2{\cdot}\overset{CO_2Et}{\overset{|}{C}}Br{\cdot}CHBr{\cdot}CO_2Et \longrightarrow CO_2H{\cdot}CH_2{\cdot}\overset{CO_2H}{\overset{|}{C}}{:}CBr{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}\overset{CO_2H}{\overset{|}{C}}H_2 + CO_2H{\cdot}CO_2H.$$

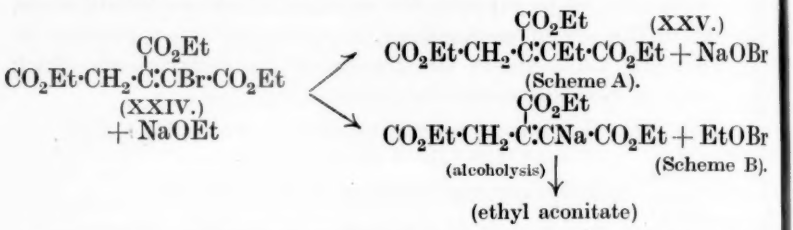
(XXIII.)

This was proved "by the ordinary tests and by analysis," but no analyses were quoted. Under the conditions of our experiments, the product is not a mixture of succinic and oxalic acids; it is aconitic acid, which can be isolated in almost quantitative yield (*vide* experimental portion, Section A).

### (c) *Reduction in a Non-aqueous Medium.*

In all the cases previously mentioned, the replacement of the halogen by hydrogen in presence of dilute alkali hydroxide leads to the formation of an alkali hypobromite in solution, and it seemed of interest to discover whether the tendency to reduction would manifest itself independently of the production of this compound. An experiment in which the aqueous alkali hydroxide was replaced by alcoholic sodium ethoxide appeared to afford a means of settling

this question, because, if the production of sodium hypobromite were the motive force of the process, a substance such as ethyl bromoaconitate (XXIV), which with sodium hydroxide yields ethyl aconitate and sodium hypobromite, when treated with sodium ethoxide should give ethyl ethylaconitate (XXV) and sodium hypobromite (Scheme A). On the other hand, if, as previously suggested, the reduction process is due to the tendency of a potentially mobile system to increase its mobility by gaining hydrogen in place of bromine, then the products should be ethyl aconitate and ethyl hypobromite (Scheme B):




So far as our experiments have gone, there can be little doubt that Scheme B actually represents the mechanism, because the product is ethyl aconitate and not ethyl ethylaconitate. Our efforts to isolate the ethyl hypobromite which must also have been formed have not so far been successful, and as the products of decomposition of this substance are somewhat difficult to isolate and recognise, we have carried out the reaction in the presence of a substance, ethyl malonate, the fate of which is much more easily ascertained, since any oxidation consequent on the reduction of the bromoaconitate must lead to the easily isolated, crystalline substance ethyl ethanetetracarboxylate, which actually was isolated in good yield along with the ethyl aconitate (experimental portion, Section E).

## EXPERIMENTAL.

### (A) *Derivatives of Aconitic Acid.*

Crystallised citric acid (500 gms.), heated with dilute sulphuric acid as described by Hentschel (*J. pr. Chem.*, 1887, [ii], **35**, 205), yielded 200 gms. of aconitic acid, and this, when esterified with 600 c.c. of absolute alcohol and 200 c.c. of sulphuric acid, gave 280 gms. of twice-distilled ethyl aconitate, b. p. 172°/18 mm.

Although ethyl aconitate readily absorbs bromine in carbon tetrachloride solution in bright sunlight (Ruhemann and Allhusen, *loc. cit.*), in winter the absorption of bromine is very slight, even in presence of a naked arc light. Ethyl αβ-dibromotricarballylate was therefore prepared by exposing ethyl aconitate to bromine

vapour (20% excess) in a desiccator for 2 or 3 weeks and removing the excess of bromine by suction or by shaking successively with sodium bisulphite and sodium carbonate (Found: Br = 37·94; 38·27. Calc., 38·28%).

*Action of Heat on Ethyl Dibromotricarballylate: Formation of the Lactone Ester of Bromohydroxytricarballylic Acid,*

$$CO_2Et\cdot CH_2\cdot \overset{CO-O}{\underset{}{C}}Br\cdot \overset{}{\underset{}{C}}H\cdot CO_2Et \quad \text{or} \quad CO_2Et\cdot CH_2\cdot \overset{O\text{———}CO}{\underset{}{C}}(CO_2Et)\cdot CHBr.$$

—On distillation under diminished pressure, the dibromo-ester at once lost ethyl bromide and passed into the bromo-lactone ester, b. p. 205°/10 mm. (Found: Br = 25·56. $C_{10}H_{17}O_6Br$ requires Br = 25·89%). No trace of aconitic ester, the formation of which by direct loss of bromine (3) (p. 2129) would at once have been observed, if it occurred, owing to the much lower boiling point of ethyl aconitate, was actually detected.

*Action of Alkalis on Ethyl αβ-Dibromotricarballylate: Formation of Aconitic Acid.*—(a) *Barium Hydroxide:* The dibromo-ester (40 gms.) was heated on the steam-bath for ½ hour with saturated barium hydroxide solution, and the barium aconitate collected. The dried salt (33 gms.; theor. 35·8 gms.), on treatment with mineral acid, yielded practically pure aconitic acid, m. p. 183° (decomp.).

(b) *Sodium Carbonate:* The dibromo-ester (53 gms.) was boiled with 500 c.c. of 2*N*-aqueous sodium carbonate, the solution was acidified with hydrochloric acid, boiled to expel carbon dioxide, made alkaline with ammonia, and treated with excess of barium chloride, alcohol being added to complete the precipitation of the barium aconitate. The acid regenerated from the barium salt melted at 183° with decomposition. The yield was 85%, 15% of the product being represented by gummy mixtures of acids which were not identified.

(c) *Methyl-alcoholic Potassium Hydroxide:* The bromo-ester (100 gms.) was heated to 100° and run in a thin stream into 150 gms. of boiling 6*N*-methyl-alcoholic potassium hydroxide. Excess of water and hydrochloric acid were added and the organic acids extracted with ether and esterified with methyl alcohol without previous purification. The main portion of the ester boiled at 160°/20 mm., and was identified as methyl aconitate by analysis (Found: C = 49·07; H = 5·42. Calc., C = 48·70; H = 5·45%) and by hydrolysis to aconitic acid. The aconitic acid can also be isolated by way of the barium salt as in experiment (b) above. The yield is 90%, the remaining material being obtained as an uncrystallisable gum.

The aconitic acid obtained in the course of the above experi-

ments was in each case identified by direct comparison and a mixed-melting-point determination with a genuine specimen, and by analysis (*e.g.*, Found: C = 41·1; H = 3·7. Calc., C = 41·4; H = 3·4%).

*Action of Cold Sodium Ethoxide on Ethyl αβ-Dibromotricarballylate: Formation of Ethyl α-Bromoaconitate.*—The dibromo-ester was treated with alcoholic sodium ethoxide (1 mol.) in the cold, the alcohol was evaporated, the residue mixed with ether, and the sodium bromide (wt. theor.) removed. From the ethereal filtrate an oil was obtained, b. p. 194°/20 mm. (without decomp.) (contrast the dibromo-ester) (Found: Br = 24·0. $C_{12}H_{17}O_6Br$ requires Br = 23·7%).

*Action of Alkalis on Ethyl α-Bromoaconitate: Formation of Aconitic Acid.*—These experiments were carried out in exactly the same way as those with the dibromotricarballylic ester, and the results were in every way identical.

(B) *Derivatives of the Alkylglutaconic Acids.*

These experiments need only be outlined, as they are similar in most respects to the experiments on derivatives of aconitic acid (section A).

(a) *α-Methylglutaconic Acid.*—The normal form of this acid (m. p. 145°) was prepared by Thole and Thorpe's method (J., 1911, **99**, 2196) from the methylation product of ethyl sodiodicarboxyglutaconate. It was converted into its dibromide by exposing the dry, finely-powdered solid to bromine vapour for 24 hours.

*αβ-Dibromo-α-(or -γ-)methylglutaric acid* crystallises from chloroform–benzene in lustrous prisms, m. p. 178° (decomp.) (Found: Br = 53·1. $C_6H_8O_4Br_2$ requires Br = 52·6%).

*Reduction in presence of alkalis.* On boiling the acid for a short time with dilute alkali hydroxides a solution was formed from which, on working up for organic acids in the usual way, a crystalline product was obtained. This, when drained from the adhering gummy impurities and crystallised from ether, consisted of normal α-methylglutaconic acid, m. p. 145° (direct comparison; mixed-melting-point determination).

(b) *β-Methylglutaconic Acid.*—The normal form of this acid (m. p. 149°) was prepared by hydrolysis of ethyl *iso*dehydracetate and converted into its dibromide by the bromine vapour method (above).

*αβ-Dibromo-β-methylglutaconic acid* melts at 142° after crystallisation from chloroform–light petroleum (Found: Br = 52·7. $C_6H_8O_4Br_2$ requires Br = 52·6%).

*Reduction by alkalis.* On treating with alkalis as in the preceding experiment, a solid product was obtained which, when crystallised from ethyl acetate–light petroleum, melted at 115°, and was identified as the labile form of β-methylglutaconic acid (direct comparison; mixed-melting-point determination). Despite careful search, the normal isomeride (m. p. 149°) could not be found.

(C) *Derivatives of Dialkylglutaconic Acids.*

(a) *αβ-Dimethylglutaconic acid* was prepared from ethyl α-methylacetoacetate and ethyl cyanoacetate by Rogerson and Thorpe's method (J., 1905, **87**, 1699). The dibromide was not prepared by the bromine vapour process, loss of hydrogen bromide too readily following the absorption of bromine. All attempts to brominate in solvents led to the production of uncrystallisable gums.

*α-Bromo-αβ (or -βγ)-dimethylglutaconic Acid.*—Finely-powdered αβ-dibromoglutaconic acid was exposed to bromine vapour until the evolution of hydrogen bromide ceased. The solid product was freed from excess of bromine by exposure over potassium hydroxide in an evacuated desiccator, and then crystallised from benzene–chloroform, from which small prisms separated, m. p. 115° (decomp.) (Found: Br = 33·4. $C_7H_9O_4Br$ requires Br = 33·7%).

(b) *αγ-Dimethylglutaconic acid* was prepared by Thole and Thorpe's method (J., 1911, **99**, 2198). Unlike the αβ-dimethyl acid, this acid readily absorbs bromine vapour without losing hydrogen bromide.

*αβ-Dibromo-αγ-dimethylglutaric acid* crystallises from benzene and melts at 134° (Found: Br = 50·3. $C_7H_{10}O_4Br_2$ requires Br = 50·3%). The action of alkalis on this acid and the preceding bromo-acid gave rise to hydroxylation products only, and in neither case could the presence of a glutaconic acid be detected.

(D) *Static Unsaturated Acids.*

(a) *Vinylacetic Acid.*—Ethyl βγ-dibromobutyrate (the dibromide of ethyl vinylacetate) was prepared from allyl cyanide by Lespieau's method (*Bull. Soc. chim.*, 1905, **33**, 55; *Compt. rend.*, 1905, **133**, 63). On hydrolysis with aqueous barium hydroxide (compare section A) it yielded βγ-dihydroxybutyric acid, which was isolated in the form of its *barium* salt (Found: Ba = 36·4. $C_8H_{14}O_8Ba$ requires Ba = 36·6%), and identified by the formation of butenolactone (Found: C = 57·0; H = 4·9. Calc., C = 57·1; H = 4·8%) on distillation of the free acid. Vinylacetic acid could not be detected in the hydrolysis product.

(b) *Crotonic Acid.*—Ethyl dibromobutyrate was prepared by

direct addition of bromine to ethyl crotonate in carbon tetrachloride solution. On boiling with dilute alkali hydroxides it was converted quantitatively into bromocrotonic acid, m. p. 106° (Found : Br = 48·1. Calc., Br = 48·5%). No reduction to crotonic acid could be detected.

(c and d) $\Delta^1$-cyclo*Hexeneacetic and* cyclo*Hexylideneacetic Acids.*— The dibromides of these two acids when quite pure melt at 121° and 141° respectively, higher, therefore, than the temperatures given in the literature. On treatment with dilute alkalis, they undergo deep-seated decompositions the products of which are still under investigation. In neither case, however, could the formation of either *cyclo*hexene- or *cyclo*hexylidene-acetic acid be detected, although had any appreciable quantity of either been produced it could easily have been isolated.

(E) *Spontaneous Reduction in Alcoholic Solution.*

A general description of the experiments belonging to this section has already been given in the introduction. To supplement that account, the following description of a typical experiment is appended.

A well-cooled solution of sodium ethoxide (2 gms. of sodium, 25 gms. of absolute ethyl alcohol) was cautiously mixed with a solution in 40 gms. of absolute alcohol of 29·5 gms. of ethyl bromoaconitate and 14 gms. of ethyl malonate. After the spontaneous development of heat had ceased, the mixture was heated on the steam-bath for 30 minutes, and then cooled, poured into water, and extracted with ether. On drying and evaporating the extract, an oil was obtained which on distillation yielded a little unchanged ethyl malonate together with a large fraction, b. p. 140—200°/20 mm., consisting of a mixture of ethyl aconitate and ethyl ethanetetracarboxylate. By fractional distillation and freezing out the fractions, most of the ethyl ethanetetracarboxylate was readily separated, and the liquid residue then boiled at 178—185°/20 mm., and consisted of nearly pure ethyl aconitate, which was identified by the formation of a practically quantitative yield of pure aconitic acid on hydrolysis. The aconitic acid and ethyl ethanetetracarboxylate were each identified by direct comparison and mixed-melting-point determinations with authentic specimens.

Our thanks are due to the Salters' Institute for a Fellowship which has enabled one of us to take part in this investigation.

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SOUTH KENSINGTON. [*Received, June 4th,* 1924.]

# CCLXXXII.—*Studies on the Walden Inversion. Part VIII. The Influence of the Solvent on the Sign of the Product in the Conversion of β-Hydroxy-β-phenylpropionic Acids into β-Bromo-β-phenylpropionic Acids.*

By George Senter and Allan Miles Ward.

The sign of rotation of the phenylaminoacetic acid resulting from the reaction of ammonia in various solvents with phenylchloro- or phenylbromo-acetic acid is dependent on the solvent employed (Senter and Drew, J., 1915, **107**, 638; 1916, **109**, 1091; Senter and Tucker, J., 1918, **113**, 140). On the other hand, no Walden inversion occurs when α-bromo-β-phenylpropionic acid is converted into α-amino-β-phenylpropionic acid, using the same series of solvents employed in the case of the phenylhalogenoacetic acids (Senter, Drew, and Martin, J., 1918, **113**, 151).

In continuation of this work, the influence of the solvent has now been studied in the conversion of the β-hydroxy-β-phenylpropionic acids into the β-bromo-acids by means of hydrogen bromide. The solvents employed in the previous work—water, alcohols, nitriles—were, with the exception of water, inapplicable for the present reaction. The nitriles formed crystalline additive compounds with hydrogen bromide, whilst in alcoholic solution the optimum conditions existed for esterification of the β-hydroxy-acid, no β-bromo-acid being produced even at room temperature.

McKenzie and Humphries (J., 1910, **97**, 121) found that, in the conversion of *d*- and *l*-β-hydroxy-β-phenylpropionic acids into the β-bromo-β-phenylpropionic acids in aqueous solution, the sign of the resulting β-bromo-acid was opposite to that of the initial β-hydroxy-acid, and that the bromo-acid consisted of a mixture of active and racemic acids, the relative proportions being dependent on the conditions of the reaction as regards temperature and time of reaction. In the present series of experiments, a similar reversal of sign was observed in all the solvents investigated. The results are shown in the following table, the letter after the solvents indicating the experiment referred to in the experimental portion of the paper.

The table shows that the activity of the bromo-acid varies widely with the solvent employed, and also, for the same solvent, very considerably with the experimental conditions. In this connexion the experiments in formic and acetic acid solutions are of special interest. The results of experiments 1a, 1b, and 1c (p. 2141) are

| Solvent. | Sign of β-hydroxy-acid. | [α] of β-bromo-acid. | Solvent. | Sign of β-hydroxy-acid. | [α] of β-bromo-acid. |
|---|---|---|---|---|---|
| (1) Formic acid (a) | *l* | +24·4° | (4) Butyric acid. | *d* | −12·4° |
| ,, (b). | *l* | +13·3 | (5) Dichloroacetic acid. | *l* | + 1·1 |
| ,, (c). | *l* | + 9·7 | (6) Ethyl acetate. | *d* | −10·1 |
| (2) Acetic acid (a). | *l* | + 1·9 | (7) Ethyl chloroformate. | *l* | +13·5 |
| ,, (b). | *d* | −59·3 | (8) Diethyl ether. | *d* | α = − 0·49 |
| ,, (c). | *d* | −65·2 | (9) Chloroform. | *d* | −13·9 |
| ,, (d). | *l* | +28·1 | (10) Nitromethane. | *l* | + 0·59 |
| (3) Propionic acid (a). | *l* | +47·2 | (11) Nitrobenzene. | *l* | +11·4 |
| ,, (b). | *d* | − 8·4 | | | |

quite striking and show how dependent, in this conversion, are the relative proportions of the optical isomerides produced on the experimental conditions, the mere variation of passing hydrogen bromide through the formic acid solution of the hydroxy-acid instead of dissolving the hydroxy-acid in a solution of hydrogen bromide in formic acid leading to a product in the former case possessing less than half the activity of that obtained in the latter. The bromo-acid is practically insoluble in formic acid, and this probably accounts for the comparatively small racemisation of the bromo-acid on standing in contact with the formic acid hydrogen bromide solution for a longer period.

Results of a similar character to the above were obtained in the corresponding acetic acid experiments (see p. 2142). The relative racemisation of the bromo-acid on allowing the acetic acid solution to stand was, however, much greater than in the case of the formic acid solution. The bromo-acid is considerably more soluble in acetic acid than in formic acid, the relative amount of bromo-acid crystallising from the formic acid solution being much higher than from the acetic acid solution, so that this may account for the greater racemisation produced in the acetic acid experiments. It is thus evident that the hydrogen bromide (or its ions) acts as a racemising agent in the formation of the bromo-acid, and it would also appear from the above results that a catalytic racemisation of the bromo-acid by the hydrogen bromide (or its ions) takes place after the bromo-acid is formed. This was further shown by keeping a solution of the bromo-acid ($[\alpha] = -59{\cdot}3°$) in glacial acetic acid, previously saturated with hydrogen bromide, at room temperature for 3 days. At no time was a completely homogeneous solution obtained, some bromo-acid remaining undissolved throughout, but the activity of the bromo-acid had fallen at the end of this time to $[\alpha] = -7{\cdot}3°$.

The conditions of experiment were dependent on the nature of the solvent in the cases of the other solvents employed. If hydrogen bromide were only sparingly soluble in the solvent, it became

necessary to pass the gas through a solution of the hydroxy-acid in the solvent, and from a comparison with the analogous formic and acetic acid experiments this may account for the low activity of some of the bromo-acids (for example, from dichloroacetic acid and nitromethane).

The bromo-acids isolated from acetic acid solution were of much higher activity than those isolated from aqueous solution by McKenzie and Humphries (*loc. cit.*). A study of the effect of temperature on the conversion of the hydroxy- into the bromo-acid in glacial acetic acid, previously saturated with hydrogen bromide at room temperature, showed that, for a fixed time of reaction ($\frac{1}{2}$ hour), the yield of bromo-acid increased with rise of temperature, but that the activity of the product fell off rapidly as the temperature of reaction was increased (see Table, p. 2142). By carrying out the reaction at 20°, as in the previous experiments, but the time of reaction being 1 hour, a bromo-acid with specific rotation slightly less than that obtained at 25° with time of reaction $\frac{1}{2}$ hour was isolated in about equal yield. When unsaturated solutions of hydrogen bromide in glacial acetic acid were used, the yield of bromo-acid fell off rapidly with diminishing concentration of hydrogen bromide for a fixed temperature, and so no advantage was to be gained by this procedure. The best conditions for the conversion of the hydroxy- into the bromo-acid were thus found to be at 25° in 10% solution of the hydroxy-acid in glacial acetic acid solution (previously saturated with hydrogen bromide at room temperature), when a bromo-acid with $[\alpha] + 51{\cdot}6°$ was obtained in 74% yield, as compared with the bromo-acid of highest activity ($[\alpha]_D + 32{\cdot}2°$) isolated by McKenzie and Humphries in the direct conversion in aqueous solution.

*Discussion of Results.*

Although, in all the solvents investigated, the resultant β-bromo-β-phenylpropionic acid and the initial β-hydroxy-β-phenylpropionic acid were of opposite sign, the conditions of the reaction were not such as to allow a strict comparison of the magnitudes of the rotations of the bromo-acids produced. The sign of the rotation is, however, the important factor for the present purpose, although it would appear that the mechanisms of racemisation and the Walden inversion, if not identical, are closely related, and the solutions of the two problems are interdependent.

Up to the present, a Walden inversion has been effected by solvent variation in the cases of phenylbromoacetic acid and phenylchloroacetic acid (*loc. cit.*), but not in those of α-bromo-β-phenylpropionic acid (*loc. cit.*) and β-hydroxy-β-phenylpropionic acid. Thus it is

only in the single instance in which the phenyl and the carboxyl group are both attached to the asymmetric carbon atom that a variation of the solvent has been found sufficient to induce a Walden inversion; when either phenyl (as in β-hydroxy-β-phenylpropionic acid) or carboxyl (as in α-bromo-β-phenylpropionic acid) alone is attached to the asymmetric carbon atom, an inversion is not so produced. Further experiments on this aspect of the subject are being made.

The catalytic racemisation of β-bromo-β-phenylpropionic acid by hydrogen bromide in glacial acetic acid solution cannot be explained by a tautomeric change due to the migration of the hydrogen atom from the asymmetric carbon atom to the carboxyl group, for the intermediate compound $C_6H_5\cdot CBr\cdot CH_2\cdot C(OH)_2$, if formed, would give rise only to the initial isomeride on the hydrogen atom changing back. The later development of this theory by McKenzie and Smith (J., 1922, **121**, 1348), involving the formation of an unstable additive compound of the racemising agent and the carboxylic acid and its subsequent conversion into an inactive tautomeric ethylenic form, is equally inapplicable to the present case. The phenyl group is undoubtedly capable of existence in tautomeric forms, and by assuming the intermediate stage to be, for example, $\begin{matrix}H\\H\end{matrix}\!>\!C\!<\!\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}\!>\!C{:}CBr\cdot CH_2\cdot CO_2H$, the present catalytic racemisation can be brought into line with the above theory. There is, however, no more evidence for a second tautomeric form of this acid than there is in the cases studied by McKenzie. The mechanism $C_6H_5\cdot CHBr\cdot CH_2\cdot CO_2H \rightleftharpoons C_6H_5\cdot CH{:}CH\cdot CO_2H + HBr$ would fit the facts equally well, and seems more probable than the above, for this equilibrium does actually exist, and if only a minute amount of cinnamic acid were present at equilibrium, the bromo-acid would in time be converted into the inactive form.

## Experimental.

*Preparation of* d- *and* l-β-*Hydroxy*-β-*phenylpropionic Acids.*—*r*-β-Bromo-β-phenylpropionic acid was prepared from cinnamic acid and fuming hydrobromic acid by Fittig and Binder's method (*Annalen*, 1879, **195**, 131); good yields were obtained, however, only when the ice-cold reactants were again saturated with hydrogen bromide after mixture. The crude acid was well washed with cold water and converted without further purification into β-hydroxy-β-phenylpropionic acid by boiling with water.

The resolution of *r*-β-hydroxy-β-phenylpropionic acid was readily effected with morphine by the method of McKenzie and Humphries

(*loc. cit.*). The *l*-acid had m. p. 115—116°, and $[\alpha]_{Hg}^{15°}$ — 19·8° in alcohol ($c = 4·726$, $l = 2$). The *d*-acid, m. p. 116°, had $[\alpha]_{Hg}^{16°}$ + 19·8° in alcohol ($c = 4·220$, $l = 2$) (compare McKenzie and Humphries, *loc. cit.*).

*Conversion of* d- *and* l-β-*Hydroxy*-β-*phenylpropionic Acids into* β-*Bromo*-β-*phenylpropionic Acids.*

*Method of Experiment.*—In all cases hydrogen bromide was used for the conversion, but the method employed depended on the solvent under investigation. A solvent which readily dissolves hydrogen bromide (1a, 1b, 2a, 2b, 2c, 3a, 3b, 4, 6, 8, and 9) was saturated with the dry gas, and added to the active hydroxy-acid to give a 10% solution, unless otherwise stated (in general, 0·5 gm. of hydroxy-acid and 5 c.c. of solution were employed). For solvents in which hydrogen bromide is only sparingly soluble (5, 7, 10, and 11), and also in experiments 1c and 2d, the active hydroxy-acid was dissolved in the pure solvent to give a 5% solution (cases 5, 7, 10, and 11) or a 10% solution (cases 1c and 2d), which was then saturated with hydrogen bromide and kept in a closed vessel for a definite period. The resulting bromo-acid, which is very sparingly soluble in cold water, was isolated in the case of solvents which are miscible with water (experiments 1, 2, 3, 4, and 5) by pouring the products of reaction into some 150 c.c. of water at room temperature, any unchanged hydroxy-acid remaining in solution. Solvents which are immiscible with water (experiments 6, 7, 8, 9, and 10) were evaporated in a current of dry air, usually at or slightly above room temperature, and the residual bromo-acid was washed with cold water and dried over concentrated sulphuric acid in a vacuum desiccator.

All measurements of rotation were made in ethyl-alcoholic solution in a 2-dcm. tube, with the yellow mercury line.

Preliminary experiments with inactive materials showed that the conversion proceeded satisfactorily in these solvents.

(1) *Formic Acid.*—(a). The *l*-hydroxy-acid dissolved rapidly to a clear solution, and the bromo-acid separated shortly. After ½ hour, as no further separation appeared to be taking place, the bromo-acid was isolated. Yield 88%; $[\alpha]^{15°}$ + 24·4°, $c = 2·130$.

(b). Experiment as under (a), except that the time of standing before isolation of the bromo-acid was 4 days. Yield 82%; $[\alpha]^{18·5°}$ + 13·3°, $c = 2·069$.

(c). The *l*-hydroxy-acid was dissolved in formic acid and hydrogen bromide passed through the solution until saturation was reached, when all the bromo-acid appeared to have separated. The whole

operation occupied about 15 minutes. The bromo-acid was isolated at once. Yield 80%; $[\alpha]^{15°} + 9{\cdot}7°$, $c = 2{\cdot}118$.

(2) *Acetic Acid.*—(a). The *l*-hydroxy-acid dissolved fairly rapidly to give a clear solution. Precipitation of the bromo-acid from this solution was by no means so complete as from the formic acid solution. No immediate separation took place, but after 24 hours a fair crop of crystals had separated. The mixture was kept for 4 days at room temperature, and the bromo-acid then isolated. Yield 86%; $[\alpha]^{17} + 1{\cdot}9°$, $c = 2{\cdot}162$.

(b). Experiment as under 2 (a), using *d*-hydroxy-acid, except that the product was isolated after ½ hour, when the hydroxy-acid had dissolved and the solution remained clear. Yield 63%; $[\alpha]^{18°} - 59{\cdot}3°$, $c = 2{\cdot}303$.

(c). *d*-Hydroxy-acid was dissolved in glacial acetic acid–hydrogen bromide solution and maintained at 5° for 65 minutes, when the bromo-acid was isolated from the homogeneous solution. Yield 39%; $[\alpha]^{20°} -65{\cdot}2°$, $c = 1{\cdot}849$.

(d). A solution of the *l*-hydroxy-acid in glacial acetic acid maintained at 15° was saturated with hydrogen bromide (about 20 minutes), when the product was immediately isolated. Yield 17%; $[\alpha]^{15°} + 28{\cdot}1°$, $c = 0{\cdot}998$.

(e). *Effect of temperature on the activity of the product.* In each of the following experiments 0·5 gm. of *l*-hydroxy-acid ($[\alpha] - 17{\cdot}9°$) was dissolved in 5 c.c. of glacial acetic acid previously saturated with hydrogen bromide at room temperature, and the solution was maintained at a definite temperature for ½ hour, when the resultant bromo-acid was isolated. The results are recorded in the table.

| Temp. | 45° | 35° | 25° | 15° | 5° |
|---|---|---|---|---|---|
| Gm. of bromo-acid | 0·48 | 0·50 | 0·43 | 0·25 | — |
| $[\alpha]$ | +13·3° | +27·6° | +40·0° | +42·5° | — |

(f). The reaction was carried out as under (e) at 20°, but time of reaction was 1 hour. Yield 0·44 gm.; $[\alpha] + 38{\cdot}2°$, $c = 1{\cdot}794$.

(g). *Catalytic racemising effect of hydrogen bromide.* A mixture of 0·3 gm. of *l*-β-bromo-β-phenylpropionic acid ($[\alpha]^{18°} - 59{\cdot}3°$) and 3 c.c. of glacial acetic acid, saturated with hydrogen bromide, was well shaken and kept at room temperature. The bromo-acid dissolved only very slowly and at no time was a completely homogeneous solution obtained. After 3 days, the bromo-acid was isolated by pouring the mixture into 150 c.c. of water in the usual way. Yield 0·14 gm.; $[\alpha] - 7{\cdot}3°$, $c = 1{\cdot}169$.

The recovery of approximately only 50% of the original bromo-acid appears to be due to the solubility of the acid in dilute aqueous acetic acid–hydrobromic acid solution, as shown by the following experiment. The *d*-bromo-acid (0·37 gm.; $[\alpha] + 27{\cdot}6°$)

was shaken with 5 c.c. of glacial acetic acid, saturated with hydrogen bromide at room temperature, for a few minutes, and then isolated by pouring into 150 c.c. of water in the usual way. Yield 0·22 gm.; $[\alpha] + 18{\cdot}4°$, $c = 2{\cdot}201$. The loss of 0·15 gm. is in good agreement with the loss of 0·16 gm. above. The experiment also shows the active bromo-acid to be more soluble in this medium than the inactive, and so would indicate that the whole of the bromo-acid has an activity somewhat greater than $-7{\cdot}3°$.

(3) *Propionic Acid.*—(a). The *l*-hydroxy-acid dissolved readily in the propionic acid–hydrogen bromide solution, and was maintained at 25° for ½ hour. The bromo-acid then isolated was somewhat brown in colour. Yield 52%; $[\alpha]^{14°} + 47{\cdot}2°$, $c = 2{\cdot}598$.

(b). Experiment as under (a), with the *d*-hydroxy-acid. The solution was kept at room temperature for 4 days before the bromo-acid was isolated. The solution remained homogeneous at the end of this time. Yield 63%; $[\alpha]^{19{\cdot}5°} - 8{\cdot}4°$, $c = 2{\cdot}141$.

(4) *Butyric Acid.*—The butyric acid employed consisted of a mixture of *n*- and *iso*-acids. The *d*-hydroxy-acid dissolved only slowly in the butyric acid–hydrogen bromide solution, and the solution darkened in colour very considerably on standing. At the end of 2 days the liquid had separated into two layers. The upper layer was poured into 200 c.c. of water; no immediate separation of solid took place from the oil which settled to the bottom of the water, but on standing the oil slowly solidified to a yellow, somewhat pasty mass. This was filtered off and dried in the usual way. Yield 38%; $[\alpha]^{17°} - 12{\cdot}4°$.

The lower layer was poured into water and gave a yellowish-brown homogeneous solution with an ester odour. On standing, however, the smell of butyric acid became more pronounced. In addition to reaction I, it is plausible that reaction II may also occur in this case.

$$C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2H \xleftarrow{\text{I}} C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \xrightarrow{\text{II}} C_6H_5{\cdot}\underset{\displaystyle O{\cdot}CO{\cdot}C_3H_7}{\underset{|}{CH}}{\cdot}CH_2{\cdot}CO_2H$$

Hydrogen bromide is not very soluble in butyric acid, so that reaction I would not be expected to proceed very rapidly. Esterification of the butyric acid by the alcoholic hydroxyl group of the β-hydroxy-β-phenylpropionic acid (reaction II) would take place slowly under the influence of hydrogen bromide, this being in line with the gradual separation into two layers.

(5) *Dichloroacetic Acid.*—*l*-β-Hydroxy-β-phenylpropionic acid dissolves readily in dichloroacetic acid, but preliminary experiment showed that the conversion of the bromo-acid was comparatively

slow. The solution was therefore kept at room temperature for 16 hours before isolation of the product. Yield 38%; $[\alpha]^{20}$ + 1·1°, $c = 1·888$.

(6) *Ethyl Acetate.*—The *d*-hydroxy-acid (0·5 gm.) dissolved readily in 10 c.c. of ethyl acetate–hydrogen bromide solution, and the bromo-acid was isolated after 24 hours. Yield 91%; $[\alpha]$ −10·1°, $c = 2·226$.

(7) *Ethyl Chloroformate.*—The hydroxy-acid is only slightly soluble in this solvent, but conversion into the bromo-acid proceeds on passing hydrogen bromide through the suspension. The bromo-acid from the *l*-hydroxy-acid was isolated after 2 hours. Yield 86%; $[\alpha]^{20°}$ + 13·5°, $c = 2·037$.

(8) *Diethyl Ether.*—The *d*-hydroxy-acid (0·5 gm.) was dissolved in 10 c.c. of diethyl ether previously saturated with hydrogen bromide. The acid passed slowly into solution, and at the end of 10 hours the solution remained somewhat turbid. The product was then isolated, but remained pasty even after leaving in a vacuum desiccator for several days. The rotation ($\alpha$ − 0·49°) of this product was determined in ethyl alcohol. After evaporating the alcohol, the solute was obtained in definite crystalline form, although still somewhat viscous, and the melting point (120—130°) indicated that conversion into the bromo-acid had taken place.

(9) *Chloroform.*—To 0·5 gm of the *d*-hydroxy-acid were added 10 c.c. of chloroform previously saturated with hydrogen bromide at room temperature. Slow dissolution was followed by considerable precipitation. The bromo-acid was isolated after 20 hours. Yield 88%; $[\alpha]^{22°}$ − 13·9°, $c = 1·760$.

(10) *Nitromethane.*—A rapid stream of hydrogen bromide was passed through a suspension of the *l*-hydroxy-acid in nitromethane for 40 minutes, and the bromo-acid was isolated after 3 hours. Yield 90%; $[\alpha]^{19°}$ + 0·59°, $c = 1·692$.

(11) *Nitrobenzene.*—The *l*-hydroxy-acid (0·5 gm.) did not dissolve at all readily in 10 c.c. of nitrobenzene, but, on passing hydrogen bromide, a clear solution was obtained and finally solid separated. After 5 hours, the hydrogen bromide was removed in a current of dry air, and the crystals were dried in a vacuum desiccator, washed with water, and again dried. Yield 67%; $[\alpha]^{16°}$ + 11·4°, $c = 1·716$.

One of us (A. M. W.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant during the course of this investigation.

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# CCLXXXIII.—*The Action of Hydrazines on Semicarbazones. Part I.*

By MARGARET MILLEN JEFFS SUTHERLAND and FORSYTH JAMES WILSON.

IT has been shown by Pinner (*Ber.*, 1887, **20**, 2358) that carbamide and phenylhydrazine react with elimination of ammonia and formation of α-phenylsemicarbazide. This work has been extended to carbamide derivatives by Skinner and Ruhemann (J., 1888, **53**, 550). Borsche (*Ber.*, 1901, **34**, 4299; 1904, **37**, 3177; 1905, **38**, 831) found that semicarbazones reacted on heating with arylamines with evolution of ammonia and formation of δ-arylsemicarbazones.

The interaction of the semicarbazones of acetophenone, benzophenone, and acetone with phenylhydrazine in the heat has now been investigated: the reactants were employed in equimolecular quantities in presence of a solvent, usually toluene. In the first two cases, the reaction proceeded according to the scheme $CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}NHPh =$ $NH_3 + CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh$, with formation of a *δ-anilinosemicarbazone*, hydrolysis of which with dilute hydrochloric acid gave the ketone and *δ-anilinosemicarbazide hydrochloride*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh,HCl$, whilst excess of more concentrated acid led to complete rupture into ketone, hydrazine hydrochloride, phenylhydrazine hydrochloride, and carbon dioxide.

To prove the correctness of the scheme outlined above, δ-anilinosemicarbazide was synthesised by heating β-carbethoxyphenylhydrazine with hydrazine hydrate in a sealed tube, $NH_2{\cdot}NH_2 + CO_2Et{\cdot}NH{\cdot}NHPh = NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh + EtOH$. It gave a hydrochloride identical with that obtained by the hydrolysis of the δ-anilinosemicarbazone with dilute hydrochloric acid, and the two preparations of the hydrochloride gave with benzaldehyde the same *benzaldehyde-δ-anilinosemicarbazone*. δ-Anilinosemicarbazide and its derivatives reduced Fehling's solution and gave black colorations or precipitates with copper sulphate.

While these two semicarbazones reacted with phenylhydrazine in a manner analogous to the experiments of Borsche, acetonesemicarbazone behaved quite differently, the reaction, even under varied conditions, being essentially one of displacement, acetonephenylhydrazone being formed and semicarbazide, or its decomposition products, being liberated. $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}NHPh = CMe_2{:}N{\cdot}NHPh + NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$; a small quan-

tity of *acetone-δ-anilinosemicarbazone* was produced, but the yield never exceeded 10 per cent. of the theoretical.

This work will be continued.

## Experimental.

*Acetophenonesemicarbazone and Phenylhydrazine.*—The semicarbazone (10 gms.) and phenylhydrazine (6 gms.) were heated under reflux in 30 c.c. of dry toluene at 120° till the evolution of ammonia ceased. The crystalline mass obtained on cooling was recrystallised several times from absolute alcohol, *acetophenone-δ-anilinosemicarbazone* separating in small, colourless needles, m. p. 210°, sparingly soluble or insoluble in solvents other than hot alcohol (Found : N = 21·01, 21·07. $C_{15}H_{16}ON_4$ requires N = 20·89 %). No other product was isolated from the toluene mother-liquors.

Acetophenone-δ-anilinosemicarbazone was hydrolysed by heating on the water-bath for several hours with 10 per cent. hydrochloric acid (1 mol.), an oil separating. The dried ethereal extract of the cooled liquid on evaporation yielded acetophenone. The aqueous portion was evaporated under reduced pressure, the crystalline residue washed with dry ether and recrystallised from absolute alcohol, from which *δ-anilinosemicarbazide hydrochloride* separated in leaflets, m. p. 193° (decomp.) (Found : Cl = 17·72. $C_7H_{10}ON_4$,HCl, requires Cl = 17·53 %). The substance, especially when moist, readily became coloured on exposure to air, and was sparingly soluble or insoluble in solvents other than water. The *benzylidene* derivative, prepared by treating the hydrochloride with benzaldehyde in alcoholic solution, crystallised from acetone in colourless, glistening needles, m. p. 206° (Found : N = 22·25, 22·26. $C_{14}H_{14}ON_4$ requires N = 22·05 %). It was sparingly soluble or insoluble in the usual solvents except acetone; hydrolysis with dilute hydrochloric acid gave benzaldehyde and the hydrochloride mentioned above.

*δ-Anilinosemicarbazazide.*—β-Carbethoxyphenylhydrazine (2·25 gms.) (Heller, *Annalen*, 1891, **263**, 278), hydrazine hydrate (1·25 gms.), and alcohol (10 c.c.) were heated in a sealed tube at 150—200° for 3 hours. After cooling, and evaporation under reduced pressure, the residue was recrystallised from absolute alcohol, *δ-anilinosemicarbazide* separating in colourless needles, m. p. 151° (Found : N = 33·80, 33·81. $C_7H_{10}ON_4$ requires N = 33·73 %), soluble in water or hot alcohol. The hydrochloride, colourless leaflets from alcohol, m. p. 193°, prepared by evaporating a solution in dilute hydrochloric acid under reduced pressure, was identical with the hydrochloride already described.

*Benzophenonesemicarbazone and Phenylhydrazine.*—Dry toluene

(50 gms.) containing 10 gms. each of the semicarbazone and phenylhydrazine was boiled till no more ammonia was evolved. The crystalline substance deposited on cooling and standing was washed with toluene and dried. The toluene mother-liquors on evaporation under reduced pressure left a brown syrupy residue which crystallised on addition of a little absolute alcohol; the solid was washed with a little alcohol and dried. These two united products after several recrystallisations from absolute alcohol gave 12 gms. of *benzophenone-δ-anilinosemicarbazone*, colourless, silky needles, m. p. 161° (Found : N = 16·80, 17·08. $C_{20}H_{18}ON_4$ requires N = 16·96%), insoluble in water and easily soluble in hot alcohol. The alcoholic mother-liquors on concentration gave a small quantity of benzophenonephenylhydrazone, formed apparently by displacement, and also a small quantity of a high-melting, water-soluble substance which was not identified.

Benzophenone-δ-anilinosemicarbazone was hydrolysed in the usual way with dilute hydrochloric acid, and benzophenone was identified in the form of its oxime; the δ-anilinosemicarbazide hydrochloride was identical with the one already described and gave the same benzylidene derivative.

On heating with excess of 12 % hydrochloric acid complete decomposition into benzophenone, hydrazine hydrochloride, phenylhydrazine hydrochloride, and carbon dioxide took place. The products were identified by conversion into the oxime, benzalazine, benzaldehydephenylhydrazone, and by means of lime-water, respectively.

*Acetonesemicarbazone and Phenylhydrazine.*—Toluene (40 c.c.) containing 5 gms. of each reactant was boiled for 4 hours. Ammonia was evolved and, on cooling, a white, crystalline solid separated which was collected and extracted with hot alcohol, in which the greater part was insoluble. The alcoholic solution on concentration deposited semicarbazide, colourless prisms, m. p. 96° (Found : N = 55·94, 56·20. Calc., N = 56·00 %); the substance insoluble in alcohol was identified as hydrazodicarbonamide, a decomposition product of semicarbazide. The toluene filtrate was concentrated under reduced pressure to small bulk, and the small quantity of solid that separated on cooling and standing, recrystallised from alcohol, gave colourless needles of *acetone-δ-anilinosemicarbazone*, m. p. 169° (Found : N = 27·28, 27·35. $C_{10}H_{14}ON_4$ requires N = 27·18 %). The toluene was then completely removed under reduced pressure and the residual oil was identified as acetonephenylhydrazone by its boiling point and by hydrolysis with acid. The reaction was repeated, varying the concentrations and employing higher temperatures with solvents such as xylene and a

paraffin boiling at 160°; the action was, however, essentially the same throughout, the yield of the anilinosemicarbazone being always small. This substance was soluble in hot alcohol, sparingly soluble or insoluble in other solvents. Heating with dilute hydrochloric acid effected hydrolysis into acetone and δ-anilinosemicarbazide hydrochloride, identical with previous specimens.

In conclusion, we wish to express our thanks to the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

[*Received, May 16th*, 1924.]

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## CCLXXXIV.—*The Dehydration of the Optically Active Methyl- and Ethyl-hydrobenzoins.*

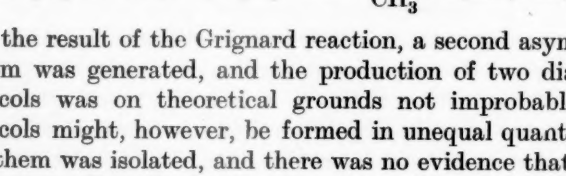
By ALEX. MCKENZIE and ROBERT ROGER.

THE object of the present research was to examine the dehydration of certain glycols whose optically active forms can be synthesised, and whose products of dehydration may possibly be optically active.

When *l*-benzoin was acted on by magnesium methyl iodide, a dextrorotatory glycol was obtained (McKenzie and Wren, J., 1910, **97**, 473), the nomenclature *l*-αβ-dihydroxy-αβ-diphenylpropane being assigned to it for the purpose of indicating its configurative relationship to the parent ketol:

$$l\text{-}C_6H_5\cdot CO\cdot \overset{*}{C}H(OH)\cdot C_6H_5 \rightarrow \begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!\overset{*}{C}(OH)\cdot \overset{*}{C}H(OH)\cdot C_6H_5.$$

As the result of the Grignard reaction, a second asymmetric carbon atom was generated, and the production of two diastereoisomeric glycols was on theoretical grounds not improbable. Those two glycols might, however, be formed in unequal quantities; only one of them was isolated, and there was no evidence that the other had been formed at all. Taking *l*-benzoin as the reference type, the above dextrorotatory methylhydrobenzoin should have one of the alternative configurations:




The present inquiry was started with the object of throwing some

light on this subject, and in any case of deciding whether optical activity would be retained when the glycol undergoes dehydration. In the event of the dehydration pursuing the course

will the resulting methyldeoxybenzoin (which contains an asymmetric carbon atom) be optically active, or will the optical activity disappear in the molecular turmoil involved? Again, in the event of water being eliminated from the two hydroxyl groups with the formation of the diethylenic oxide, $O<^{CHPh\cdot CMePh}_{CMePh\cdot CHPh}>O$ (compare Mlle Lévy, *Bull. Soc. chim.*, 1921, [iv], **29**, 865), there is the possibility that optical activity might persist in this instance also, since the configuration of an oxide of this type can exhibit molecular asymmetry. On the other hand, if the conditions were such that the product was either diphenylmethylacetaldehyde, $CPh_2Me\cdot CHO$, or diphenylmethylvinyl alcohol, $CPhMe{:}CPh\cdot OH$, then obviously no optical activity would be apparent.

Again, *l*-benzoin had been converted by means of magnesium ethyl iodide into *l*-αβ-dihydroxy-αβ-diphenylbutane (McKenzie and Wren, *loc. cit.*), and this dextrorotatory ethylhydrobenzoin thus presents an analogous problem.

The first observations on the dehydration of *r*-methylhydrobenzoin are recorded by Tiffeneau and Dorlencourt (*Compt. rend.*, 1906, **143**, 126; *Ann. Chim. Phys.*, 1909, [viii], **16**, 237), who by the use of dilute sulphuric acid obtained an oil which was ultimately identified as diphenylmethylacetaldehyde. Subsequently Tiffeneau and Orékhov (*Compt. rend.*, 1920, **171**, 400; *Bull. Soc. chim.*, 1921, [iv], **29**, 422) ascertained that the course of the reaction is entirely altered when concentrated sulphuric acid is substituted for the dilute acid as the dehydrating agent. In this case methyldeoxybenzoin is quoted as being the sole product, the yield being 78 per cent. of the theoretical. This result was confirmed by Mlle Lévy (*loc. cit.*), who also isolated, by acting on the glycol with dilute sulphuric acid (*d* 1·51), a compound (m. p. 169°) which had previously been obtained by Tiffeneau and Dorlencourt (*loc. cit.*) by the aid of phosphoric anhydride as the dehydrating agent. This third product of the dehydration of *r*-methylhydrobenzoin is, according to Mlle Lévy, a diethylenic oxide (*loc. cit.*); it is converted into diphenylmethylacetaldehyde when it is distilled at the ordinary pressure in the presence of a trace of sulphuric acid, whereas methyldeoxybenzoin is formed by the action of concentrated sulphuric acid on it.

The present authors (this vol., p. 844) were led to study the dehydration of *r*-methylhydrobenzoin for the reason already given, and also as a sequel to the work of McKenzie and Richardson (J., 1923, **123**, 79), who had found that the action of nitrous acid on β-hydroxy-αβ-diphenylpropylamine led to the formation of a substance (m. p. 59—59·5°). The latter substance is not the methyldeoxybenzoin described by Tiffeneau, Orékhov and Mlle Lévy as melting at 58—59°, but is the isomeric *as*-diphenylacetone (m. p. 58·5—59·5°). From our experience on the dehydration of *r*-methylhydrobenzoin with concentrated sulphuric acid, *r*-methyldeoxybenzoin melts at 50—52°, and this melting point was not raised by prolonged crystallisation. Moreover, *r*-methyldeoxybenzoin forms two semicarbazones melting at 214—215° and 159—160° respectively and its formation from the glycol is accompanied by the production of a small proportion of *as*-diphenylacetone.

We now find that a mixture of diphenylmethylacetaldehyde and the *r*-diethylenic oxide (m. p. 171—172°) is produced by the action of hot dilute sulphuric acid on *r*-methylhydrobenzoin.

By the action of dilute sulphuric acid on *r*-ethylhydrobenzoin, Tiffeneau and Dorlencourt (*loc. cit.*) obtained αα-diphenylbutaldehyde. Using concentrated sulphuric acid, Orékhov (*Bull. Soc. chim.*, 1919, [iv], **25**, 182) isolated ethyldeoxybenzoin (m. p. 56—57°) and a second product (m. p. 32—33°) which was subsequently identified as diphenylbutanone (Tiffeneau and Orékhov, *loc. cit.*). Mlle Lévy obtained the diethylenic oxide, $O<\begin{matrix}CHPh\cdot CEtPh\\CEtPh\cdot CHPh\end{matrix}>O$ (m. p. 136—137°), by the action of dilute sulphuric acid on the glycol (*loc. cit.*).

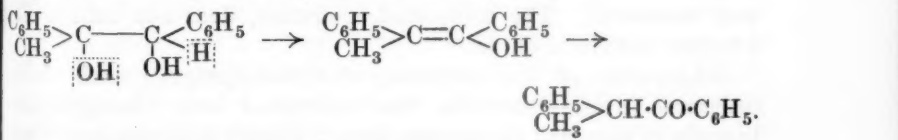
Under the conditions quoted in the experimental part, *r*-ethylhydrobenzoin gave a mixture of diphenylbutanone and the *r*-diethylenic oxide when hot, moderately dilute sulphuric acid was employed as the dehydrating agent. The oxide under the influence of concentrated sulphuric acid gave a mixture of diphenylbutanone and *r*-ethyldeoxybenzoin, whereas Mlle Lévy found diphenylbutanone only. When *l*-methylhydrobenzoin was dehydrated with concentrated sulphuric acid, *r*-methyldeoxybenzoin (m. p 50—51·5°) was isolated. On the other hand, the optical activity was retained when the dehydration was conducted with dilute sulphuric acid, since a lævorotatory diethylenic oxide (m. p. 183—184°) was isolated. This was easily obtainable in an optically pure condition, and gave $[\alpha]_D$—76·2° for $c = 2·1$ in benzene; there was no evidence that any of the racemic isomeride was produced along with it. When, however, it underwent isomeric change under the influence of concentrated sulphuric acid, the

resulting product was completely inactive, and consisted of *r*-methyldeoxybenzoin.

This is not, however, the first occasion on which *l*-methylhydrobenzoin has been dehydrated. In the course of his striking researches on carboligase, Neuberg has recently found that the addition of benzaldehyde to a fermenting solution of sugar or pyruvic acid led not only to benzyl alcohol but also to the lævorotatory ketol, $C_6H_5{\cdot}CH(OH){\cdot}CO{\cdot}CH_3$. The dextrorotatory glycol, formed by the action of magnesium phenyl bromide on this ketol, proved to be identical with the *l*-methylhydrobenzoin described by McKenzie and Wren. In order to obtain further evidence regarding the constitution of the latter glycol, Neuberg and Ohle (*Biochem. Z.*, 1922, **127**, 327) boiled it with dilute sulphuric acid, and obtained a colourless oil which was converted into a semicarbazone (m. p. 193—194°). They are in error, however, when they draw the conclusion that their oil consisted of methylphenylacetophenone (methyldeoxybenzoin). They apparently isolated the semicarbazone of diphenylmethylacetaldehyde which, according to Tiffeneau and Dorlencourt (*Ann. Chim. Phys.*, 1909, [viii], **16**, 237), melts at 192°. Neuberg and Ohle make no reference to any polarimetric examination of their oil.

The behaviour of *l*-ethylhydrobenzoin towards dilute sulphuric acid is also described in the present paper. The diethylenic oxide obtained by the action of dilute sulphuric acid melted at 167—168°, and had $[\alpha]_D$ −106·9° for $c = 1{\cdot}165$ in benzene. Concentrated sulphuric acid brings about a transformation which is mainly semipinacolinic, since diphenylbutanone is the main product, and this cannot exhibit optical activity. It seems that the other product of the transformation, namely ethyldeoxybenzoin, is formed as the inactive isomeride.

The formation of *r*-methyldeoxybenzoin from *l*-methylhydrobenzoin is not inconsistent with the mechanism of vinyl dehydration advanced by Tiffeneau and Orékhov for the action of concentrated sulphuric acid on glycols when a substituted vinyl alcohol is suggested as an intermediate phase in the dehydration :



Our result harmonises equally well, however, with the conceptions of Meerwein and of Favorski. We are, nevertheless, inclined to take the view that the dehydration with concentrated sulphuric acid involves the intermediate formation of the lævorotatory

diethylenic oxide, which then undergoes optical inactivation in its conversion into *r*-methyldeoxybenzoin. On the experimental side, there are two points which favour this view. First, it has been shown that the ethylenic oxide actually undergoes the transformation mentioned. Secondly, the crude product from the dehydration showed a slight lævorotation which cannot be due to the original glycol, which is dextrorotatory.

## EXPERIMENTAL.

*Dehydration of* r-αβ-*Dihydroxy*-αβ-*diphenylpropane*.—A mixture of 20 gms. of this *r*-methylhydrobenzoin (prepared from *r*-benzoin and magnesium methyl iodide, Tiffeneau and Dorlencourt, *Ann. Chim. Phys.*, 1909, [viii], **16**, 237; McKenzie and Wren, J., 1910, **97**, 473) and 360 gms. of dilute sulphuric acid (equal weights of concentrated sulphuric acid and water) was boiled for 2¼ hours, the resulting oil extracted with ether–benzene, and the extract dried. On removal of the solvent, light petroleum (b. p. 40—60°) was added to the semi-solid residue, the solid was removed, and crystallised from benzene–ethyl alcohol. The diethylenic oxide separated in rhombic plates, m. p. 171–172° (yield 4 gms.) (Found: C = 85·7; H = 6·7. Calc., C = 85·7; H = 6·7%). The other product of this action was diphenylmethylacetaldehyde, which was purified by distillation under diminished pressure (semicarbazone, m. p. 194—195°; oxime, m. p. 121—122°). Under somewhat different conditions, Mlle Lévy isolated the oxide only. A similar result was obtained by the application of phosphoric anhydride (10 gms.) on the glycol (10 gms.), when 2·4 gms. of the oxide were isolated.

Our experience with the action of concentrated sulphuric acid on the glycol has already been recorded (this vol., p. 844).

We found no evidence for the formation of an amino-alcohol when the oxide was heated with aqueous ammonia, since the oxide was recovered unchanged. Nor was it acted on by magnesium methyl iodide. When 4 gms. were heated for 23 hours with the Grignard reagent prepared from 30 gms. of methyl iodide, 3·5 gms. were recovered. The compound, therefore, does not behave like a typical ethylenic oxide.

*Dehydration of* l-αβ-*Dihydroxy*-αβ-*diphenylpropane with Dilute Sulphuric Acid*.—*l*-Benzoin was converted into *l*-methylhydrobenzoin by means of magnesium methyl iodide (McKenzie and Wren, *loc. cit.*).

This dextrorotatory glycol (4·5 gms.) with $[\alpha]_D$ + 34° in acetone was gradually added with continuous trituration to 70 c.c. of dilute sulphuric acid (*d* 1·55). It was slowly transformed into a brown,

pasty mass. After remaining for 4 hours at the ordinary temperature, water was added, and the product was extracted with benzene. After drying, the bulk of the benzene was removed, and ethyl alcohol was added. The solid (2·3 gms.) which separated was crystallised from benzene–ethyl alcohol until its rotation attained to a constant value.

l-*Di-diphenylmethylethylene oxide*, $\left(\begin{matrix}\text{CPhMe·CHPh}\\ \text{└—O—┘}\end{matrix}\right)_2$, crystallises in diamond-shaped plates, m. p. 183—184°, whereas the inactive oxide melts at 171—172° [Found : C = 85·5; H = 6·8; *M* (cryoscopic method in benzene = 412. $(C_{15}H_{14}O)_2$ requires C = 85·7; H = 6·7%; M = 420]. It is readily soluble in benzene and chloroform, moderately soluble in acetone and light petroleum, and sparingly soluble in ethyl alcohol. As distinct from the dextrorotatory glycol from which it was prepared, the compound gives a lævorotation. In chloroform : $l = 2$, $c = 2{\cdot}2905$, $\alpha_D^{15°} - 3{\cdot}52°$, $[\alpha]_D^{15°} - 76{\cdot}8°$. In benzene : $l = 2$, $c = 2{\cdot}1000$, $\alpha_D^{13°} - 3{\cdot}20°$, $[\alpha]_D^{13°} - 76{\cdot}2°$.

There was no alteration in rotatory power when 4 drops of alcoholic potash (1 gm. of caustic potash in 10 c.c. of alcohol) were added to a solution of the oxide in benzene giving $\alpha_D - 3{\cdot}40°$ ($l = 2$). After 24 hours the rotation was unchanged.

The semicarbazone (*m.* p. 195—196°) of diphenylmethylacetaldehyde was obtained from the oil remaining after the removal of the oxide by treating it with semicarbazide.

*Transformation of the* l-*Diethylenic Oxide into* r-*Methyldeoxybenzoin.*—The powdered oxide (1 gm.) was triturated with 20 c.c. of concentrated sulphuric acid, a purple coloration appearing, and after 5 hours the mixture was poured into 300 gms. of ice and water. The temperature fell to −7°. The solid (0·9 gm.) obtained by extraction with ether was crystallised from aqueous alcohol. The resulting methyldeoxybenzoin, m. p. 49—51°, showed no optical activity when polarimetrically examined in ethyl-alcoholic solution.

*Dehydration of* l-αβ-*Dihydroxy*-αβ-*diphenylpropane by Concentrated Sulphuric Acid.*—The powdered glycol (6 gms.) was gradually added (30 minutes) with continuous trituration to 60 c.c. of concentrated sulphuric acid. After 2½ hours the mixture was poured into ice and water, and the product extracted with ether. Yield = 5·4 gms. After four crystallisations from light petroleum the crystals melted at 49—50·5°, and the slight red coloration with concentrated sulphuric acid indicated the presence of a trace either of the glycol or of the oxide. 0·8 Gm. was made up to 20 c.c. with ethyl alcohol, and the solution was slightly *lævorotatory*, giving $\alpha_D - 0{\cdot}09°$ ($l = 2$). After several crystallisations from aqueous ethyl

alcohol, silky needles of methyldeoxybenzoin (m. p. 50—51·5°) were obtained. These were quite inactive, and gave the characteristic pale yellowish-green coloration with concentrated sulphuric acid.

*Dehydration of* r-αβ-*Dihydroxy*-αβ-*diphenylbutane with Dilute Sulphuric Acid.*—The oil, which was obtained by dehydrating this glycol (prepared from *r*-benzoin and magnesium ethyl iodide; Acree, *Amer Chem. J.*, 1905, **33**, 193) under the same experimental conditions as in the case of *r*-methylhydrobenzoin, consisted of a mixture of the diethylenic oxide and diphenylbutanone. The former, which was precipitated by the addition of light petroleum, separated from ethyl alcohol in plates, m. p. 137—138°. The oily residue after the removal of the oxide was distilled under diminished pressure, and the distillate was acted on by semicarbazide. The semicarbazone obtained melted at 194—195° (Orékhov gives 191—192°) (Found : C = 72·8; H = 6·5. Calc., C = 72·6; H = 6·8%). The ketone obtained by decomposing the semicarbazone by dilute sulphuric acid melted at 35—36° (Found : C = 85·7; H = 7·3. Calc., C = 85·7; H = 7·2%).

The diethylenic oxide (2 gms) was added gradually to concentrated sulphuric acid (20 gms.) at 0°. After 25 minutes, the mixture was poured into ice and water, and extracted with ether. The resulting oil solidified on the addition of a nucleus of ethyldeoxybenzoin. Light petroleum (b. p. 40—60°) was added and the residue (0·9 gm.) collected. After one crystallisation from light petroleum, needles of ethyldeoxybenzoin (m. p. 55—57°) separated. The presence of diphenylbutanone in the remaining filtrate was also shown by the isolation of its semicarbazone (m. p. 194—195°).

*Dehydration of* l-αβ-*Dihydroxy*-αβ-*diphenylbutane with Dilute Sulphuric Acid.*—This glycol (3·5 gms.; prepared from *l*-benzoin and magnesium ethyl iodide, McKenzie and Wren, *loc. cit.*) was dehydrated in practically the same way as the propane homologue (p. 2152). The product after dilution was extracted with ether-benzene. The oily residue obtained from the washed, dried extract was crystallised from ethyl alcohol. Yield 1·4 gms.

l-*Di-diphenylethylethylene oxide*, $\left(\begin{array}{c}\text{CPhEt·CHPh}\\ \text{└—O—┘}\end{array}\right)_2$ separates from benzene–ethyl alcohol in rhombic plates, m. p. 167—168°, whereas the inactive isomeride melts at 137—138° [Found : C = 85·8; H = 7·2; *M* (cryoscopic method in benzene) = 444. $(C_{16}H_{16}O)_2$ requires C = 85·7; H = 7·2%; *M* = 448). The oxide is easily soluble in benzene or chloroform, moderately soluble in acetone or light petroleum, and sparingly soluble in ethyl alcohol. Its specific

rotatory power was determined in chloroform: $l = 2$, $c = 2{\cdot}125$, $\alpha_D^{17^\circ} = -3{\cdot}89^\circ$, $[\alpha]_D^{17^\circ} - 91{\cdot}5^\circ$. In benzene: $l = 2$, $c = 1{\cdot}165$, $\alpha_D^{15{\cdot}5^\circ} -2{\cdot}49^\circ$, $[\alpha]_D^{15{\cdot}5^\circ} - 106{\cdot}9^\circ$.

The dextrorotatory *l*-ethylhydrobenzoin thus gave a lævorotatory diethylenic oxide.

*Conversion of* l-*Di-diphenylethylethylene Oxide into* r-*Ethyldeoxybenzoin.*—One gram of the *l*-diethylenic oxide was triturated with 20 c.c. of concentrated sulphuric acid, when a reddish-purple coloration appeared. After 5 hours at the ordinary temperature, the mixture was poured into ice and water. After extraction with ether, 0·2 gm. of ethyldeoxybenzoin, m. p. 53—55°, was separated from its mixture with diphenylbutanone. This showed no optical activity when examined polarimetrically in ethyl-alcoholic solution.

We are indebted to the Department of Scientific and Industrial Research, and to the Carnegie Trust for their generous assistance.

UNIVERSITY COLLEGE, DUNDEE.
UNIVERSITY OF ST. ANDREWS. [*Received, June 24th,* 1924.]

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## CCLXXXV.—*Influence of Substituents on Chemical and Physical Properties: the Velocity of Reaction between Substituted Benzoic Anhydrides and an Aliphatic Alcohol.*

By HAROLD GORDON RULE and THOMAS RAMSAY PATERSON.

SUBSTITUTION in an organic compound has been compared to the introduction of an electrical doublet which varies in orientation and strength with the nature of the ingoing group (J. J. Thomson, *Phil. Mag.*, 1923, [vi], **46**, 497). The doublet representing a positive group such as $NO_2$ or $CO_2H$ is found to be of the opposite orientation to that representing a negative one such as $CH_3$, OH or Cl. Further, the change in chemical reactivity following on substitution is traced to the change in the electrical field in and around the molecule.

As many properties of compounds are influenced by the electrical state of the molecule, it might be expected that there would be some regularity in the manner in which they are affected by different substituents. By the use of a method based on the views of J. J. Thomson the relative polarity of certain substituents has been deduced from their influence on the inductive capacity of non-polar compounds (Rule, this vol., p. 1121). In this way, there is

first obtained the series (I) $NO_2$,CN,OH,Cl,Br,I,OMe,($CH_3$,H), which represents progressively diminishing polar *magnitudes* irrespective of *sign*. This series corresponds closely to what has been termed the *general polar effect* of the substituents (Robinson, *Ann. Rep.*, 1922, p. 98) and to their influence on the dissociation constants * of acids (compare Flürscheim, J., 1909, **95**, 718). By rearrangement to represent a continuous change from high positive to high negative polarity there may be obtained the *polar series* (II) $NO_2$,CN,$CO_2$H,H,Me,I,Br,Cl,OH, which is in general agreement with the influence of the groups on benzene substitution and the optical rotation of certain *d*-amyl and *l*-menthyl derivatives (Rule, *loc. cit.*). Positive and negative groups also differ in their effect on the electromagnetic rotation of compounds. The positions in the series assumed by the hydroxyl and methoxyl groups appear to vary somewhat, the former being above the halogens in the case of inductive capacities but below them in the case of the dissociation constants (see table on p. 2159). Similarly, the methoxyl group apparently lies below the halogens in these two cases, but above them in optical rotation.

Many determinations have been made of the influence of substituents on the reactivity of a parent compound. Michael and Oechslin (*Ber.*, 1909, **42**, 317) found the rate of esterification of benzoic acid in absence of a catalyst to be influenced in the sequence $NO_2$>Cl>H>Me and compared this with the influence of the same groups on the dissociation constant of benzoic acid. From the rather involved figures of Kellas (*Z. physikal. Chem.*, 1897, **24**, 227) it may be deduced that in presence of hydrochloric acid as catalyst the esterification is affected in approximately the reverse order, H>$CH_3$>Hals.>$NO_2$. Kellas (*loc. cit.*) also examined the rate of hydrolysis of esters of mono-substituted benzoic acids, for which his figures indicate the sequence $NO_2$>Hals.>H>Me.

A more complete series of investigations has been carried out by Olivier (*Rec. trav. chim.*, 1914, **33**, 244) on the formation of sulphones from *p*-bromobenzenesulphonyl chloride and substituted benzenes, and from benzene and substituted benzene-sulphonyl chlorides. In each case, substituents affect the velocity coefficients in the order Me>H>Hals.>$NO_2$. The hydrolysis of substituted benzyl chlorides (Olivier, *ibid.*, 1923, **42**, 516, 775) gave similar results, the relative influence found being

Me>H>Hals.>$CO_2$H>$NO_2$.

* The authors' attention has recently been directed to the work of Betti (summarised in *Gazzetta*, 1923, **53**, 417) showing that in certain cases substituents have the same influence on rotatory power as on acidity.

In all the above cases it will be observed that the relative effect of a given group is in agreement with the general series (I) deduced from inductive capacities.

There is little evidence bearing on the relative influence of the methoxyl group on reactivity, although Orton and King (*Rep. Brit. Assoc.*, 1915, p. 83) have shown that the nitro- and methoxy-groups differ markedly in their effect on the chlorination of certain benzene compounds. In the present investigation, the influence of the groups $NO_2$, Cl, OMe and Me upon the reactivity of benzoic anhydride has been determined, using (*a*) an excess of ethyl alcohol, or (*b*) a molecular proportion of cetyl alcohol in benzene solution. Comparative figures for the substituents Me, OMe, and H were obtained by the former method, the velocity coefficients being calculated according to the usual expression for a monomolecular reaction. Owing to their high reactivity and low solubility the majority of the nitro- and chloro-derivatives could not be examined in this way, since in presence of the necessarily large excess of alcohol the reaction continued rapidly during analysis. The relative effect of the groups $NO_2$ and Cl as compared with H is obtained from the rate of reaction of the corresponding compounds with cetyl alcohol in benzene solution. These velocity coefficients are calculated from the expression $k' = 1/a.\ 1/t.\ x/(a\text{-}x)$, where $a$ represents the original concentration of anhydride and of cetyl alcohol, and $x$ the number of gram-molecules converted in $t$ hours. In order to retain the anhydrides and acids in solution it was necessary to work at a high dilution, and as the constants in benzene as solvent varied somewhat with the concentration, the determinations were all carried out in 0·02$N$-solution. Under these conditions the methoxy and toluic derivatives reacted with extreme slowness, but the change proceeded even more sluggishly in solvents other than hydrocarbons. Contrary to the experience of Michael and Oechslin with the esterification of the free acids, the anhydride reaction was found to be highly sensitive to the influence of substituents.

The results are collected in the following tables.

TABLE I.

Influence of Substituents on the Velocity of Reaction between Benzoic Anhydride and Ethyl Alcohol in excess, at 60°.

| | $NO_2$. | Cl. | H. | OMe. | Me. |
|---|---|---|---|---|---|
| Ortho ..... | — | 0·140 | 0·0208 | 0·0078 | 0·0086 |
| Meta ..... | (0·8) | — | | 0·029 | 0·0143 |
| Para ..... | — | — | | 0·0060 | 0·0109 |

TABLE II.

Influence of Substituents on the Velocity of Reaction between Benzoic Anhydride and Cetyl Alcohol in benzene solution, at 60°.

| | $NO_2$. | Cl. | H. |
|---|---|---|---|
| Ortho ..... | 0·103 | 0·12 | |
| Meta ..... | 0·51 | 0·55 | 0·092 |
| Para ..... | 0·86 | 0·49 | |

*General Influence of the Substituents.*

From the above figures the general influence of the substituents is seen to be $NO_2>Cl>(H,OMe)>Me$, although if the *o*-, *m*-, and *p*-derivatives are considered separately the positions of Cl and OMe vary slightly according to the isomerides compared. This sequence agrees with the order $NO_2>Cl>H>Me$ found by Michael and Oechslin for the esterification of the free benzoic acids in excess of methyl alcohol at 135°, although the actual differences found by these investigators are small.

*Correlation with other Properties of Compounds.*

Some of the series expressing the effect of substituents upon chemical reactivity to which reference has already been made may be briefly summarised :

| | |
|---|---|
| Hydrolysis of benzoic esters ..... | $NO_2>$hals.$>H>Me$ |
| Esterification of benzoic acid { no catalyst ..... | $NO_2>Cl>H>Me$ |
| Esterification of benzoic acid { HCl as catalyst | $NO_2<Cl<Me<H$ |
| Sulphone formation ..... | $NO_2<$hals.$<H<Me$ |
| Hydrolysis of benzyl chlorides ..... | $NO_2<CO_2H<$hals.$<H<Me$ |
| Ester formation from benzoic anhydride ..... | $NO_2>Cl>(H,OMe)>Me$ |

It may therefore be concluded that the influence of substituents on the reactivity of benzene derivatives is in many cases expressed approximately by the general sequence $NO_2$, $CO_2H$, halogens, (H,OMe),Me. Except for the relative positions of H and OMe, this is in close agreement with that holding for the molecular inductive capacities of mono-substituted derivatives of the benzene and paraffin series and the strengths of aliphatic and *o*-substituted benzoic acids. Hence it is probable that the same sequence also holds very nearly for the reactivity of compounds other than benzene derivatives, although the relationship may at times be masked.

A number of figures relating to the various properties under discussion are given in tabular form on p. 2159. In spite of the widely differing experimental conditions the general relationship will readily be seen.

*Influence of Substituents on Chemical and Physical Properties.*

| Property. | Figures refer to | $NO_2$. | CN. | $CO_2H$. | OH. | F. | Cl. | Br. | I. | (OEt) OMe. | H. | $CH_3$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Molecular inductive capacity.* | Series HX. | — | 37 | 22 | 15 | — | — | — | — | — | — | — |
| | $C_2H_5X$. | 21 | 19 | 2·4 (?) | 15 | — | 7·6 | 7·1 | 5·9 | (4·4) | — | — |
| | $C_6H_5X$. | 36 | 27 | — | — | — | 11 | 5·5 | — | 5·0 | 2·0 | 2·4 |
| Dissociation constants,* 25°. | Series $X{\cdot}CH_2{\cdot}CO_2H$. | — | 0·37 | 0·158 | 0·015 | — | 0·155 | 0·138 | 0·075 | 0·033 | 0·002 | 0·001 |
| | (1 : 2) $X{\cdot}C_6H_4{\cdot}CO_2H$. | 0·62 | — | 0·121 | 0·102 | — | 0·13 | 0·14 | 0·14 | — | 0·007 | 0·013 |
| Velocity of reaction. | Hydrolysis of benzyl chlorides, *p*-series (Olivier). | 0·044 | — | 0·11 | — | — | 0·47 | 0·41 | 0·37 | — | 1 | 9·4 |
| | Benzoic anhydrides, (1) *m*-series, in excess of EtOH. | (0·8) | — | — | — | — | — | — | — | 0·029 | 0·021 | 0·014 |
| | (2) *p*-Series, $C_{16}H_{33}{\cdot}OH$ in benzene. | 0·86 | — | — | — | — | 0·49 | — | — | — | 0·092 | — |
| Optical activity. | Menthyl esters of *o*-acids, $X{\cdot}C_6H_4{\cdot}CO_2H$. Difference from $[M]_D$ for H compound.† | +152° | — | +101° | — | −45° | −44° | −34° | −2° | −91° | * | −8° |
| Nitration of $C_6H_5X$.‡ | *m*-Compound, per cent. | 93 | — | 76 | | | | | | | | |
| | *p*-Compound, per cent. | | | | — | 87 | 70 | 62 | 66 | — | | 41 |

* From figures in Landolt Börnstein's "Physikalisch-chemische Tabellen" (1923). Inductive capacities refer to normal temperature and long wave-lengths.

† Cohen, J., 1914, **105**, 1892; 1918, **113**, 57.

‡ Holleman, "Die direkte Einführung von Substituenten," 1910, p. 199.

### *The Alternate Effect.*

Except in the case of certain of the *o*-anhydrides there is a definite alternate effect observable in the influence of a substituent in the *o*-, *m*-, and *p*-positions, respectively. Thus $k_m$ is greater than $k_p$ or $k_o$ for the negative substituents Me, OMe, and Cl, whereas for the positive nitro-group $k_m$ is less than $k_p$.

A point of special interest is that, although substituents affect the rate of ester formation from benzoic anhydride and free acid in the same general sense, the alternate effect in the one case is the reverse of that in the other. In the esterification of the free acids Michael and Oechslin find *m*-$NO_2$>*p*-$NO_2$>*o*-$NO_2$, and *p*-Me>*m*-Me.

The figures of Goldschmidt (*Ber.*, 1895, **28**, 3218) as corrected by Kailan (*Annalen*, 1907, **351**, 186) referring to the esterification of free acids in the presence of a catalyst indicate an alternate effect similar to that found for anhydride reaction.

Another interesting difference in ester formation is that whereas 3-nitrophthalic acid on esterification with hydrochloric acid as catalyst yields mainly the β-ester, the anhydride on boiling with alcohol gives mainly the α-ester (Marckwald and McKenzie, *Ber.*, 1901, **34**, 486). Unfortunately, all attempts to examine this point further by the preparation of a mixed *o*- and *p*-nitrobenzoic anhydride were unsuccessful.

Owing to steric hindrance and the specific effect of the solvent, it is not possible to trace any correspondence between the alternate effect of a substituent upon anhydride reaction and its position in the polar series II. It is, however, evident that the alternate effect of the methoxyl group is strongly marked. This, although not in agreement with the position of the group in the deduced polar series, is repeated in its effect upon the optical activity of amyl and menthyl derivatives (Rule, *loc. cit.*).

## Experimental.

*Solvents* were purified in the usual way. Kahlbaum's benzene "for molecular weight determination" was allowed to stand over sodium wire, distilled, and fractionated. Ethyl alcohol (abs.) was boiled under reflux over calcium filings and fractionated.

*Cetyl alcohol* (Merck), m. p. 46·5—48·5°, was twice recrystallised from absolute alcohol. After prolonged drying in a vacuum over sulphuric acid and finally in a vacuum at 40°, it melted at 49·1°. Michael and Wolgast (*Ber.*, 1909, **42**, 3175) quote 49·2°.

*Anhydrides.* A number of these are well known and were prepared and purified by standard methods. The following are new.

p-*Chlorobenzoic anhydride* was prepared by heating the acid chloride with the sodium salt of the acid. The crude product was washed successively with ligroin, concentrated aqueous sodium carbonate, a little alcohol, and finally benzene. It was then extracted with boiling benzene and filtered hot. The anhydride crystallised from benzene in thin, colourless plates, m. p. 194·8° (yield about 50%, calculated on the acid used). 0·1346 gave 0·1303 AgCl; Cl = 23·94. $C_{14}H_8O_3Cl_2$ requires Cl = 24·04%.

*p*-Chlorobenzoic anhydride is only very sparingly soluble in cold, and moderately soluble in boiling, hydrocarbon solvents. At 30° in benzene, 100 c.c. dissolve 0·76 gm. It is still less soluble in light petroleum, but more so in chloroform.

m-*Chlorobenzoic Anhydride.*—*m*-Nitrobenzaldehyde was converted into *m*-chlorobenzaldehyde by the method of Erdmann and Schwechten (*Annalen*, 1890, **260**, 58) as modified by Eichengrün and Einhorn (*ibid.*, 1891, **262**, 135), and the chloroaldehyde oxidised with potassium permanganate solution.

A solution of *m*-chlorobenzoic acid in toluene (10 parts) was boiled for 4 hours with excess of phosphoric oxide, shaken, after decantation, with dilute aqueous alkali, dried, concentrated, and treated with ligroin. The anhydride, which separated in plates, was recrystallised from light petroleum until pure; m. p. 95·5° (yield 30%; a quantity of the free acid was recovered unchanged). 0·1025 gave 0·1001 AgCl; Cl = 24·15%.

*m*-Chlorobenzoic anhydride crystallises from alcohol or light petroleum in fine, colourless needles and from benzene or toluene in plates. It is very readily soluble in benzene and chloroform, and also in alcohol, with which it reacts rapidly. It is less soluble in ligroin.

o-*Chlorobenzoic anhydride*, prepared from the acid by the method adopted for the *m*-compound, crystallised from light petroleum in microcrystalline needles, m. p. 79·6°. In solubility it resembles the meta compound. 0·1270 gave 0·1230 AgCl; Cl = 23·96%.

o-*Methoxybenzoic Anhydride.*—*o*-Methoxybenzoyl chloride was shaken with ignited sodium carbonate and pyridine for ½ hour, the reaction mixture poured on to ice, and the solid product washed with dilute hydrochloric acid and water. The crude anhydride was dissolved in chloroform and purified in the usual way. It crystallised from light petroleum in exceedingly fine needles, m. p. 72·4°. It is very soluble in benzene and chloroform. 0·1583 gave 0·3899 $CO_2$ and 0·0676 $H_2O$; C = 67·17, H = 4·74. $C_{16}H_{14}O_5$ requires C = 67·13, H = 4·90%).

m-*Methoxybenzoic anhydride*, prepared from the acid by use of phosphoric oxide and twice crystallised from light petroleum,

formed colourless plates, m. p. 66·6° (yield 44%). In solubility it resembles the *o*-isomeride.

0·1600 gave 0·3942 $CO_2$ and 0·0731 $H_2O$; C = 67·19, H = 5·08%.

*Velocity Determinations.*

These were carried out in corked tubes or well-stoppered glass bottles immersed in a thermostat. In the experiments with cetyl alcohol the reactants were present in equimolecular proportions, sufficient benzene being added to bring the concentration of each down to 0·02*N*.

Free acid was estimated by titration with sodium hydroxide, using cresol-red as indicator. Alcoholic solutions were first treated with several times their volume of light petroleum or benzene, followed by a quantity of neutralised water. Benzene solutions were titrated directly, after adding a quantity of neutralised water.

*Determinations in Excess of Ethyl Alcohol at* 60°.—All experiments were confirmed by repetition and the constants obtained ranged over 60 to 80% of the complete reaction. The following is a typical experiment, where $t$ = time in hours, $x'$ = titre in c.c. of 0·0367*N*-alkali, $a'$ = titre for complete reaction.

*Benzoic Anhydride,* 0·05*N* (5 *c.c withdrawn,* a′ = 6·82).

| | | | | | | |
|---|---|---|---|---|---|---|
| $t$ ..... | 4·33 | 5·50 | 8·67 | 24·0 | 26·0 | 29·1 |
| $x'$ ..... | 1·25 | 1·55 | 2·32 | 4·75 | 4·85 | 5·15 |
| $k$ ..... | 0·0203 | 0·0204 | 0·0208 | 0·0216 | 0·0207 | 0·0210 |
| | | | | | Mean | 0·0208 |

*Influence of Substituents on the Rate of Reaction.*

| Substit. | Extreme values. | Mean $k$. | Substit. | Extreme values. | Mean $k$. |
|---|---|---|---|---|---|
| *o*-Cl ..... | 0·136 —0·142 | 0·140 | *p*-OMe... | 0·0058—0·0064 | 0·0060 |
| *m*-$NO_2$... | 0·80 —0·83 | 0·81 | *o*-Me ... | 0·0081—0·0090 | 0·0086 |
| *o*-OMe ... | 0·0075—0·0082 | 0·0078 | *m*-Me ... | 0·0138—0·0147 | 0·0143 |
| *m*-OMe | 0·028 —0·031 | 0·029 | *p*-Me ... | 0·0105—0·0114 | 0·0109 |

Owing to the high reactivity and low solubility of *m*-nitrobenzoic anhydride in alcohol, the figure for this compound can only be regarded as approximate. For similar reasons, no satisfactory figures could be obtained for the other nitro- and chloro-derivatives.

*Determinations with Cetyl Alcohol in Benzene Solution* (0·02*N*) *at* 60°.—For benzoic anhydride, $k'$ = 0·092 (extreme range 0·090 to 0·096). The values began to rise after reaction had progressed to the extent of 18% in 115 hours. Previous addition of benzoic acid (0·5 mol.) led to the value $k$ = 0·37 at 20 hours and the values rose steadily. The *o*-derivatives quoted below gave constants over the same range as the parent compound, but the figures for *m*- and *p*-derivatives remained steady over 50 to 60% of the reaction.

Probably this difference is due to the greater catalytic activity of the *o*-acids set free.

*Influence of Substituents on the Rate of Reaction.*

| Substit. | Extreme values. | Mean *k'*. | Substit. | Extreme values. | Mean *k'*. |
|---|---|---|---|---|---|
| *o*-$NO_2$ ... | 0·102—0·104 | 0·103 | *o*-Cl ..... | 0·116—0·122 | 0·120 |
| *m*-$NO_2$... | 0·48 —0·52 | 0·51 | *m*-Cl..... | 0·53 —0·56 | 0·55 |
| *p*-$NO_2$ ... | 0·84 —0·89 | 0·86 | *p*-Cl ..... | 0·48 —0·50 | 0·49 |

(Owing to its low solubility, *p*-nitrobenzoic anhydride was used in 0·0172 *N*-solution.)

In conclusion the authors desire to thank the Department of Scientific and Industrial Research for a scholarship which has enabled one of them (T. R. P.) to take part in the above investigation, and also the Earl of Moray Fund for a grant (to H. G. R.) which has covered some of the expenses incurred.

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## CCLXXXVI.—*A Synthesis of ψ-Pelletierine.*

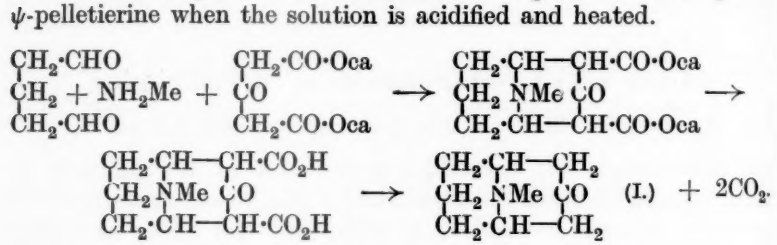
By ROBERT CHARLES MENZIES and ROBERT ROBINSON.

ψ-PELLETIERINE, the crystalline constituent of the mixture of bases obtainable from the root bark of the pomegranate (*Punica granatum* L.), was recognised by Ciamician and Silber as a ring homologue of tropinone, but the constitutional formula (I) now accepted as correct was proposed by Piccinini, who applied experimental methods and arguments similar to those which Willstätter had devised in the course of his studies in the tropine group. Considerable interest attaches to this substance, partly on account of its constitution, the peculiarities of which were exploited by Willstätter and Waser (*Ber.*, 1911, **44**, 3423) in the well-known synthesis of *cyclo*octatetraene; partly because it has served as the starting point of interesting comparisons of the pharmacological properties of derivatives of its related, stereoisomeric alcohols with corresponding derivatives of tropine and ψ-tropine; but also because the occurrence of such a compound is highly significant in relation to the problem of the origin of plant alkaloids. This subject has already been discussed (Robinson, J., 1917, **111**, 876), and it was concluded that ornithine (or a diaminoadipic acid) is elaborated so as to produce alkaloids of the pyrrolidine group such as hygrine, atropine, and cocaine, whilst bases of the piperidine series such as coniine and ψ-pelletierine are in a similar manner

derived from lysine (or a diaminopimelic acid). An important item of evidence which can be cited in favour of the ornithine theory of the genesis of the bases of the tropine group * was omitted from the memoir quoted on account of ignorance and the reference is to the occurrence of αδ-di-(dimethylamino)butane,

$$NMe_2\cdot[CH_2]_4\cdot NMe_2,$$

in *Hyoscyamus muticus* (Willstätter and Heubner, *Ber.*, 1907, **40**, 3869). The synthesis of tropinone from succindialdehyde, methylamine, and a reactive derivative of acetone (J., 1917, **111**, 762) is regarded as a laboratory summary of the complex operations which the plant performs in order to develop the tropine nucleus from ornithine. Similar processes must evidently be postulated in the phytochemical production of ψ-pelletierine from lysine or an equivalent and therefore it becomes necessary to attempt in this case also the provision of the appropriate, supposedly analogous synthesis *in vitro*. We are now able to place on record the observation that glutardialdehyde reacts with methylamine and calcium acetonedicarboxylate with formation of a product which yields ψ-pelletierine when the solution is acidified and heated.



The base itself was identified by careful comparison with an authentic specimen, and the highly characteristic *dipiperonylidene* derivative exhibited identical properties whether prepared from the synthetical or the natural product. Glutardialdehyde has been obtained from *cyclo*pentanone by a slight modification of the method of Harries and Tank (*Ber.*, 1908, **41**, 1704) and familiarity with the various processes was sought by practising the related conversion of *cyclo*hexanone into adipdialdehyde by way of *cyclo*hexene (Neresheimer, *Ber.*, 1906, **39**, 2849; Harries and v. Splawa Neymann, *ibid.*, 1908, **41**, 3557). The adipdialdehyde obtained was condensed with methylamine and calcium acetonedicarboxylate and a small amount of an oily base was ultimately isolated which

* Cuskhygrine is now regarded as an *as.*-disubstituted acetone derivative, $R_2CH\cdot CO\cdot CH_3$ (Hess and Fink, *Ber.*, 1920, **53**, [*B*], 781), but this modified view in no way affects the validity of the arguments which were based on the assumption that it belongs to the type $RCH_2\cdot CO\cdot CH_2R$ and brought forward in connexion with the genetic relationship of the base to other members of the pyrrolidine group of alkaloids.

had the properties to be anticipated in the case of a ring-homologue of ψ-pelletierine. It gave a dipiperonylidene derivative closely resembling those of tropinone and ψ-pelletierine and a methiodide, extremely sparingly soluble in alcohol and crystallising in curious regular cubic aggregates of prisms. Experiments in connexion with this substance are in progress and further description is reserved.

## Experimental.

*Adipdialdehyde and Glutardialdehyde.*—Our experiences in relation to the formation of the ozonides of *cyclo*pentene and *cyclo*hexene have confirmed at every point the descriptions of Harries and his colleagues (*loc. cit.*). The hexane employed as solvent should be as pure as possible and give only a faint cloudiness with ozone. A satisfactory material is the washed *n*-hexane supplied by Messrs. Carless, Capel, and Leonard. This was boiled during some hours over an alkaline solution of potassium permanganate and then distilled over phosphoric oxide. The b. p. was 68·6—69·0°, and almost all came over at 68·8°. In order to be able to make economical use of *cyclo*pentanone a careful comparison of the preparation of *cyclo*hexene from *cyclo*hexanone by way of *cyclo*hexanol and by way of *cyclo*hexylamine was made. The former process is already adequately described and is satisfactory, but the latter method cannot be recommended. The yields obtained are quoted in percentages of the theoretically possible: *cyclo*hexanoneoxime (crude product, 99%; recrystallised from light petroleum, 81·6%): *cyclo*hexylamine hydrochloride (88·3%, using very carefully dried alcohol; 73·7%, using ordinary absolute alcohol): *cyclo*hexyltrimethylammonium iodide (using methyl iodide alone or in presence of alkali, the yield was unsatisfactory, but almost quantitative results were obtained by the use of methyl sulphate in excess in presence of aqueous potassium hydroxide, followed by conversion of the methosulphate into the iodide): *cyclo*hexene (the yields in three experiments were 25·5, 24·8, 26·0%). The main product of the distillation of *cyclo*hexyltrimethylammonium hydroxide was *cyclo*hexyldimethylamine, and this is contrary to the statement of Skita and Rolles (*Ber.*, 1920, **53**, 1250) that the hydroxide splits up completely into *cyclo*hexene, water, and trimethylamine. *cyclo*Hexeneozonide is a relatively stable substance; after a violent hexane–oxygen explosion, which occurred in a vessel containing some, unchanged fragments of the substance were collected. The highest yield of the ozonide was 84%, the losses being due to fuming and the volatility of *cyclo*hexene. The decomposition of the ozonide is the stage of the process which is least satisfactory and the yields

recorded by Harries and Tank are very low. We have made numerous experiments with the object of effecting improvements and the best results were obtained in the following manner:

A solution of *cyclo*hexeneozonide (20 gms.) in acetic acid (285 c.c.) was gradually added with mechanical agitation to a mixture of aqueous titanous chloride (300 c.c. of 15%, 0·89*N* by titration) and sodium acetate solution (1200 c.c. of 40%). The reaction proceeded rapidly in the cold, but experiments with dilute solutions of titanous chloride and *cyclo*hexeneozonide which should theoretically have proved equivalent, volume for volume, showed that 5 c.c. of the former required 8·5 c.c. of the latter. It is evident, therefore, that even under these conditions *cyclo*hexeneozonide breaks down with the formation of carboxylic acids. The mixture was repeatedly extracted with ether and the ethereal solution washed with concentrated potassium carbonate, dried with the anhydrous reagent, filtered and, after removal of the solvent, a residue of adipdialdehyde (5·0 gms.) was obtained. From this amount of the dialdehyde, 1·0 gm. of the supposed ring homologue of $\psi$-pelletierine was derived. *cyclo*Pentene was prepared by the dehydration of *cyclo*pentanol and it may be noted that the hydrocarbon can be readily estimated in hexane solution by titration with bromine dissolved in carbon tetrachloride. The absorption is more rapid and the end point sharper than is the case with *cyclo*hexene. *cyclo*Hexeneozonide reacts instantly with titanous salts, but this was not the behaviour of *cyclo*penteneozonide and a more prolonged treatment was necessary. Under the following conditions, the yield of glutardialdehyde from the ozonide was 23% and a considerable improvement in the preparation has therefore been effected. A solution of titanium trichloride (50 c.c. containing 6·85 gm. $TiCl_3$) was mixed with slightly more, approximately 40% aqueous sodium acetate than sufficed to make the solution neutral to congo-red. *cyclo*Penteneozonide (3 gms.), dissolved in acetic acid (25 c.c.), was then introduced during 20 minutes with mechanical stirring. Agitation was continued during an hour and towards the end of this period the temperature was raised to 40° and a further equal quantity of the solution of the titanous salt added. The whole operation was conducted in an atmosphere of carbon dioxide. The reaction mixture was extracted with ether and, after removal of acetic acid by washing with aqueous potassium carbonate, evaporation of the solvent left a residue of glutardialdehyde (0·6 gm.). In this preparation very considerable difficulty arose on account of the intractable titanic acid gels, which hindered the separation of the ethereal layer. Messrs. Peter Spence and Co., Manchester Alum Works, very kindly presented us with a specimen of titanium

sulphate chloride solution which contained about twice as much tervalent titanium in 1 c.c. as the solution previously employed and had the additional advantage that the free mineral acid content was very much lower. This solution was employed in reductions of the ozonide with much gain in convenience.

*ψ-Pelletierine.*—Acetonedicarboxylic acid was recrystallised by cooling a solution in its own weight of tepid water and then dried in a vacuum. The pure acid (2·0 gms.) was dissolved in water (10 c.c.) and precipitated chalk (2·5 gms.) then added. When effervescence ceased, glutardialdehyde (from 3·0 gms. of *cyclo*penteneozonide) dissolved in water (15 c.c.) was introduced and finally aqueous methylamine (10 c.c. of 20%) was gradually added with stirring during 30 minutes. After 24 hours, the mixture was acidified with hydrochloric acid (congo-red) boiled until evolution of carbon dioxide appeared to have ceased, the cooled liquid was rendered alkaline, and the calcium precipitated by ammonium oxalate (3·0 gms. in water). The filtered solution was repeatedly extracted with ether and the combined extracts were dried by means of potassium carbonate. After removal of the solvent, a light yellow, viscous oil remained; 2·0 gms. of this crude base were obtained from 11·0 gms. of *cyclo*penteneozonide. As the yield of dialdehyde from the ozonide is about 20%, it appears that glutardialdehyde gives approximately its own weight of crude base. The latter did not crystallise and the whole quantity available (about 4 gms.) was distilled in a high vacuum. The first two drops of the distillate and the residue in the flask were alone rejected and the pale yellow liquid was mixed with acetone (2 vols.), and picric acid (0·5 gm.) added. A sparingly soluble *picrate* separated immediately in an unsatisfactory condition, but on rubbing with fresh acetone was resolved into a crystalline powder. The substance was washed with acetone, crystallised from hot water, the bright canary-yellow needles were decomposed by aqueous sodium hydroxide, and the base was extracted repeatedly by pure ether. The combined extracts were washed with a little aqueous potassium carbonate, dried with the anhydrous reagent, and the solvent evaporated. On exposure to a vacuum, the residual colourless oil crystallised and after contact with porous porcelain the substance was recrystallised from light petroleum. The soft, colourless, flaky crystals melted at 48·5°, alone or mixed with an authentic specimen of ψ-pelletierine. The synthetical product exhibited under the polarising microscope the same appearance as a similarly crystallised specimen of natural origin. The bright green colour produced by the addition of a trace of potassium dichromate to a solution of the base in sulphuric acid was identical in the case of

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both specimens and a careful comparison did not disclose any divergence of behaviour between them. The characteristic *di-piperonylidene* derivative was prepared from synthetic and natural ψ-pelletierine and the crystalline forms observed were identical, all the shapes detailed below being obtained in each case. The melting point of a mixture was again undepressed and complete identity of the substances in solubility and colour reactions was observed.

*Dipiperonylidene-ψ-pelletierine*, $\begin{matrix} CH_2\cdot CH{-}C{:}CH\cdot C_6H_3{:}O_2CH_2 \\ | \quad | \quad | \\ CH_2\ NMe\ CO \\ | \quad | \quad | \\ CH_2\cdot CH{-}C{:}CH\cdot C_6H_3{:}O_2CH_2 \end{matrix}$.

—Potassium hydroxide (0·5 gm.) dissolved in water (0·5 c.c.) was added to a solution of ψ-pelletierine (1 gm.) and piperonal (3 gms.) in ethyl alcohol (25 c.c.) and the mixture boiled during 10 minutes. Yellow crystals separated from the hot solution and, after cooling, the derivative was collected, washed with alcohol, and dried (2·5 gms.). The substance crystallises from alcohol, in which, as in most neutral organic solvents, it is very sparingly soluble, in glistening, yellow, microscopic plates having an equilateral triangular outline. When ethyl acetate was employed as solvent and cooling was rapid, the plates were hexagonal owing to small truncations of the angles. The compound also separated from alcohol and from ethyl acetate in rhombic and diamond-shaped prisms. All specimens melted at 226—227° (Found: C = 71·8; H = 5·5. $C_{25}H_{23}O_5N$ requires C = 71·9; H = 5·5%).

Dipiperonylidene-ψ-pelletierine closely resembles the related tropinone derivative and its salts with mineral acids are all sparingly soluble, deep yellow substances. The solution in concentrated sulphuric acid is very intensely royal blue and becomes green and then yellow on dilution with water.

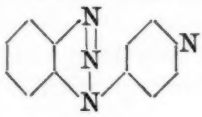
We desire to thank Professor Barger for kindly allowing us the use of an ozone generator and for other facilities, and grateful acknowledgment is also made to the Government Grant Committee of the Royal Society for a grant which has defrayed part of the expense of the investigation.

THE UNIVERSITIES OF ST. ANDREWS,
BRISTOL, AND MANCHESTER. [*Received, July 3rd*, 1924.]

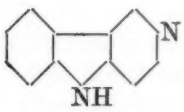
# CCLXXXVII.—5-*Carboline and some Derivatives.*

By Robert Robinson and Sidney Thornley.

Four bases, $C_{11}H_8N_2$, containing benzene, pyrrole, and pyridine nuclei fused in the order named should exist and of these 3-carboline has recently been obtained by Lawson, Perkin, and Robinson (this vol., p. 626), whilst 4-carboline (norharman) is a product of degradation of harmine (Kermack, Perkin, and Robinson, J., 1921, **119**, 1602), and of evodiamine (Asahina, *J. Pharm. Soc. Japan*, 1924, No. 503, 1) and has also been synthesised. Quindoline (Fichter and Rohner, *Ber.*, 1910, **43**, 3489) is a benzo-6-carboline, but the nuclear arrangement characteristic of 5-carboline does not occur in any substances hitherto described. The method of preparation of the latter base which is now placed on record suffers from the disadvantage that the initial material is somewhat difficult of access, but the novel stages proceed in an entirely satisfactory manner. 4-Chloropyridine and *o*-phenylenediamine react at 100° with formation of the hydrochloride of *N*-γ-pyridyl-*o*-phenylenediamine, which is converted by the action of nitrous acid into 1-γ-pyridylbenzotriazole (I). This is a far stronger base than 1-α-pyridylbenzotriazole (Lawson, Perkin, and Robinson, *loc. cit.*), but like the latter it may be distilled in a vacuum without decomposition. Considerable difficulty was experienced in effecting the decomposition of this triazole into nitrogen and 5-carboline (II), until it was observed that the change proceeded smoothly on strongly heating with syrupy phosphoric acid.



(I.)



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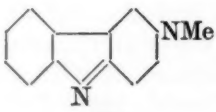
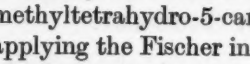


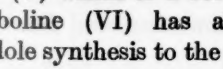
(III.)

This method may also be conveniently utilised in the preparation of 3-carboline from 1-α-pyridylbenzotriazole and in the analogous synthesis of quinindoline; it is doubtless of wide applicability. 5-Carboline is a strong and stable base; its methosulphate is decomposed by alkaline hydroxides with formation of 5-methyl-5-*iso*carboline (III), a pale yellow, crystalline substance which reacts with water to form 5-carboline methohydroxide. The anhydrobase forms a colourless methosulphate (IV) which on treatment with aqueous sodium hydroxide yields no ether-soluble base. The fluorescence exhibited by 5-carboline and its methyl derivatives is much weaker than that characteristic of the bases of the 4-carboline series.

On reduction with sodium and *n*-butyl alcohol 5-carboline yields a tetrahydro-derivative (V) which is a secondary base. A pentamethyltetrahydro-5-carboline (VI) has also been obtained by applying the Fischer indole synthesis to the phenylmethylhydrazone of triacetonamine.



(IV.)



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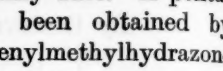


(VI.)

## EXPERIMENTAL.

*Preparation* of 4-*Chloropyridine.*—The methods which we have employed in the various stages are indicated by the following references and comments.

Acetonedioxalic ester—Willstätter and Pummerer (*Ber.*, 1904, **37**, 3734); chelidonic acid—Claisen (*Ber.*, 1891, **24**, 111); chelidamic acid—Haitinger and Lieben (*Monatsh.*, 1885, **6**, 285); 4-hydroxypyridine—Lerch (*Monatsh.*, 1884, **5**, 402); 4-chloropyridine—Haitinger and Lieben (*loc. cit.*). Acetone (78 gms.) and diethyl oxalate (430 gms.) gave chelidonic acid (137·5 gms.), chelidamic acid (126 gms.), 4-hydroxypyridine (57·3 gms.), and 4-chloropyridine (40 gms.). In the last stage of the preparation, an ethereal solution of 4-chloropyridine is obtained. This is dried over potassium hydroxide, and a column must be employed in the fractionation, since otherwise considerable amounts of the base will be carried over by the ether. 4-Chloropyridine has b. p. 41°/13 mm., 49°/18 mm.

4-Hydroxypyridine was recovered unchanged after being heated (oil-bath at 190°) during 33 hours with phosphorus pentachloride (3 mols.) and a little phosphoryl chloride.

N-γ-*Pyridyl*-o-*phenylenediamine*, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_5H_4N$.—A mixture of 4-chloropyridine (20·4 gms.) and *o*-phenylenediamine (21 gms.) was heated at 98°/40 mm. during 2½ hours. The liquid became crimson and gradually more viscous; after 2 hours, crystallisation commenced and at the end of the period mentioned the material had almost completely solidified. Since, however, chloropyridine was still refluxing, the reaction was continued during 1¼ hours at 140° under the same pressure. The filtered solution of the product in hot dilute hydrochloric acid was rendered alkaline with sodium hydroxide, and the brown precipitate crystallised from boiling water (animal charcoal). The yield of dry crystallised material was 20·4 gms. This substance is sparingly soluble in cold water, chloroform, or acetone, moderately readily soluble in the

hot solvents, and very readily soluble in ethyl alcohol. It crystallises from methyl alcohol in elongated prisms, m. p. 173·5° (Found : C = 71·2; H = 6·0. $C_{11}H_{11}N_3$ requires C = 71·4; H = 5·9 %), and from much hot benzene in needles. The *hydrochloride* is extremely sparingly soluble in boiling ethyl alcohol and is deposited in slender, microscopic needles when concentrated hydrochloric acid is added to an alcoholic solution of the amine and the liquid is heated. The substance is unchanged by prolonged treatment with hot acetic acid, but when a solution of the base in absolute formic acid was boiled during 6 hours, a new compound, doubtless γ-pyridylbenziminazole, was formed. This base was unchanged by nitrous acid and crystallised from light petroleum in well-shaped hexagonal tablets, m. p. 123°.

1-γ-*Pyridylbenzotriazole* (I).—Under conditions similar to those described below, 1 gm. of pure *N*-γ-pyridyl-*o*-phenylenediamine gave 1·35 gms. of the crude hydrated triazole derivative and this after crystallisation weighed 1·28 gms. The process, therefore, proceeds in an almost quantitative manner. The isolation of pyridylphenylenediamine is, however, not only unnecessary but disadvantageous. The condensation product from 4-chloropyridine (11·6 gms.) and *o*-phenylenediamine (11 gms.) was dissolved in 10 per cent. hydrochloric acid (250 c.c.) and, the temperature being kept below 10°, a solution of sodium nitrite (12·4 gms.) in water (125 c.c.) gradually introduced. Colourless needles were deposited and after a few hours these were collected. The substance is the *hydrochloride* of pyridylbenzotriazole and may be crystallised from methyl alcohol in needles, m. p. 262° (decomp.). It is insoluble in benzene, but soluble in cold water to a solution which is acid to litmus. The addition of sodium hydroxide to the aqueous solution of the hydrochloride and to the filtrate from this salt gave a bulky precipitate which was collected, washed with water, and dried in the air (15·1 gms.). The substance crystallises from hot water in slender, colourless needles which melt at 82° to an obscure liquid which clears at 105° and simultaneously evolves steam. Air-dried material lost all its water of crystallisation in a vacuum over sulphuric acid (Found : loss = 21·5. $C_{11}H_8N_4,3H_2O$ requires $H_2O$ = 21·6%. The anhydrous base crystallised from benzene–light petroleum in colourless plates, m. p. 113·5° (Found : C = 67·2; H = 4·0. $C_{11}H_8N_4$ requires C = 67·3; H = 4·1%). It is sparingly soluble in light petroleum and readily soluble in methyl alcohol or benzene. The substance has well-developed basic character and is very stable. It may be distilled in small quantities without decomposition and readily sublimes in slender, silky needles.

5-*Carboline* (II).—Anhydrous 1-γ-pyridylbenzotriazole (3 gms.)

along with syrupy phosphoric acid (30 c.c., $d = 1{\cdot}75$) was rapidly heated with agitation over a free flame. The pale yellow solution gradually darkened and nitrogen and steam were evolved. The completion of the reaction was judged by the cessation of the evolution of gas and the solution had then assumed a dull cherry-red colour. The base liberated from the cooled and diluted solution by means of sodium hydroxide was rendered to ether and removed from the separated extract by washing with successive small volumes of dilute hydrochloric acid. These acid solutions were made strongly alkaline and the cream-coloured precipitate was washed and dried (yield 55 %). The substance crystallises from aqueous methyl alcohol in colourless, glistening, prismatic needles and from methyl alcohol, in which it is very readily soluble, in prisms, m. p. 225° (Found : C = 78·4; H = 4·8. $C_{11}H_8N_2$ requires C = 78·6; H = 4·8 %). The base is readily soluble in alcohol, and sparingly soluble in benzene or water. It crystallises from the latter in slender needles. It is very stable and distils without decomposition under the atmospheric pressure. No coloration is developed with Ehrlich's reagent in alcoholic solution or with vanillin and concentrated hydrochloric acid. The neutral and acid aqueous or alcoholic solutions of the base do not fluoresce in ordinary light, but a solution in alcoholic hydrochloric acid exhibits bluish-violet fluorescence in the light of burning magnesium.

Crystals of 5-carboline deposited from methyl alcohol were kindly examined by Mr. G. Greenwood of the Department of Crystallography in this University, who makes the following report :

*System* : Monoclinic, holohedral. $a : b : c = 0{\cdot}8043 : 1 : 0{\cdot}4285$; $\beta = 68°46'$.

*Forms observed :* The predominating forms are $c = \{001\}$, $m = \{110\}$, and $s = \{\bar{2}11\}$. The faces $n = \{120\}$, $b = \{010\}$, and $p = \{\bar{1}11\}$, though developed to a less extent occur, very frequently.

*Crystallographic angles.*

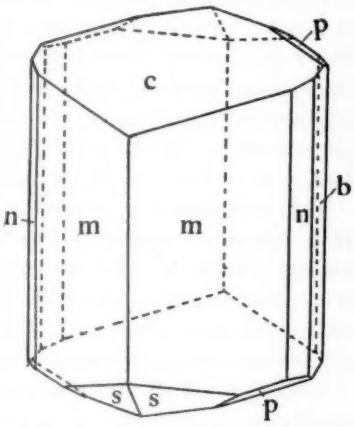
| Angle. | No. of measurements. | Limits. | Mean. Obs. | Mean. Calc. |
|---|---|---|---|---|
| (110) : (1$\bar{1}$0) | 11 | 73° 2′—74° 6′ | 73° 43′ | * |
| (010) : ($\bar{2}$11) | 10 | 70 35—71 59 | 71 6 | * |
| ($\bar{1}$10) : ($\bar{2}$11) | 8 | 48 51—49 47 | 49 28 | * |
| (110) : (001) | 25 | 72 24—73 27 | 72 53 | 73° 9′ |
| (010) : ($\bar{1}$11) | 2 | 45 39—45 45 | 45 42 | 45 44 |
| (001) : ($\bar{1}$11) | 7 | 37 46—38 39 | 38 19 | 38 17 |
| (001) : ($\bar{2}$11) | 6 | 60 5—60 38 | 60 25 | 60 6 |
| (110) : (120) | 3 | 19 2—20 47 | 19 41 | 19 27 |

The characteristic *hydrogen oxalate* was prepared in the first place in moderately concentrated solution and crystallised from hot water in flat, elongated prisms, m. p. 226° (decomp.) (Found :

C = 60·5; H = 3·9. $C_{13}H_{10}O_4N_2$ requires C = 60·5; H = 3·9 %). When a solution in hot dilute aqueous oxalic acid is quickly cooled, very symmetrical stellate clusters of short, microscopic needles separate.

The *picrate* crystallises in canary-yellow needles, m. p. 250°, on mixing hot solutions of the base and picric acid in acetone.

The *methosulphate*. 5-Carboline (4 gms.), dried at 105°, was dissolved as far as possible in boiling acetone (150 c.c.), and neutral methyl sulphate (6 gms.) in acetone (100 c.c.) gradually added. The methosulphate separated immediately in colourless crystals, and after boiling during 15 minutes the mixture was cooled and the derivative collected, washed with acetone, and dried (6·4 gms.). The substance crystallises well from ethyl alcohol in needles and from methyl alcohol in prisms (Found: in material dried at 105°, C = 52·9; H = 4·8. $C_{13}H_{14}O_4N_2S$ requires C = 53·1; H = 4·8 %). This methosulphate melts at 161° and does not exhibit fluorescence in aqueous solution. The bluish-violet fluorescence of an alcoholic solution is just perceptible in daylight and bright in the light of burning magnesium.




*5-Methyl-5-isocarboline* (III).—5-Carboline methosulphate (2 gms. in water) was added to a large excess of hot concentrated aqueous potassium hydroxide, the mixture shaken with hot benzene (800 c.c.), and the yellow upper layer dried over potassium hydroxide, first roughly by means of sticks and then by boiling the decanted liquid over the powdered reagent. The filtered solution, concentrated to about 150 c.c., deposited pale yellow needles, which were washed with benzene and dried in a high vacuum. Analysis indicated a content of water not corresponding to any simple molecular ratio and in an attempt to dehydrate the substance it was found to sublime at 138° in a high vacuum as pale yellow needles, m. p. 203—204° (Found: C = 78·7; H = 5·6. $C_{12}H_{10}N_2$ requires C = 79·1; H = 5·5 %). This hygroscopic base imparts an alkaline reaction to cold distilled water. It is soluble in hot water to a strongly alkaline solution which doubtless contains 5-carboline methohydroxide.

The crystalline *methosulphate* (IV) separates immediately (yield theoretical) when methyl sulphate is added to a well-dried benzene

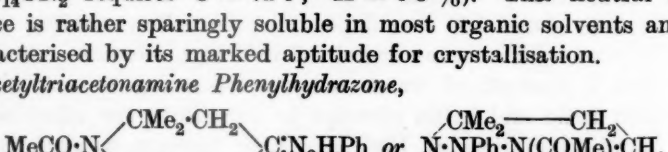
solution of the base. The salt is readily soluble in hot methyl alcohol and separates, on cooling, in colourless needles, m. p. 210—211° (Found : in material dried at 105°, C = 54·5; H = 5·3. $C_{14}H_{16}O_4N_2S$ requires C = 54·5; H = 5·2 %). The aqueous and alcoholic solutions exhibit a bluish-violet fluorescence in the light of burning magnesium. When an aqueous solution, not too dilute, is treated with potassium hydroxide, a colourless precipitate is thrown down. This is insoluble in ether and benzene but soluble in water and is not decomposed by boiling aqueous potassium hydroxide. Its behaviour is, accordingly, in striking contrast with that of 5-carboline methosulphate.

3 : 4 : 5 : 6-*Tetrahydro-5-Carboline* (V).—Sodium (24 gms.) was gradually added in large pieces to a boiling solution of 5-carboline (4·7 gms.) in *n*-butyl alcohol (250 c.c.), heating being unnecessary. After dissolution, and removal of the butyl alcohol with steam, the crystalline precipitate was washed with water, dried (4·4 gms.), and crystallised from ethyl alcohol, separating in small, colourless prisms, m. p. 215·5° with slight previous shrinking (Found : C = 76·5; H = 7·0. $C_{11}H_{12}N_2$ requires C = 76·7; H = 7·0 %).

This substance is a strong base, forming readily soluble salts. It is sparingly soluble in water, acetone, or benzene, moderately readily soluble in methyl or ethyl alcohol. With Ehrlich's reagent it gives a solution which is rose-pink when hot and yellow when cold, and with vanillin and concentrated hydrochloric acid a red coloration, which becomes bluer on boiling, is produced.

5-*Acetyl*-3 : 4 : 5 : 6-*tetrahydro-5-carboline* is readily obtained by dissolving tetrahydro-5-carboline in acetic anhydride, a considerable portion crystallising; the mixture is then added to dilute hydrochloric acid, to hydrolyse acetic anhydride. The solid crystallises from ethyl alcohol in colourless, slender needles, m. p. 254·5° with previous softening (Found : C = 72·7; H = 6·5. $C_{13}H_{14}ON_2$ requires C = 72·9; H = 6·5 %). This neutral substance is rather sparingly soluble in most organic solvents and is characterised by its marked aptitude for crystallisation.

*Acetyltriacetonamine Phenylhydrazone*,



—When a solution of triacetonamine and phenylhydrazine (equal mols.) in acetic acid was boiled during 3 hours, no indole derivative was obtained. The crude oily product was treated with cold acetic anhydride, and a clear solution obtained on the addition of dilute hydrochloric acid. A readily solidifying oil, precipitated by excess of sodium acetate, was crystallised from ethyl alcohol and

benzene; from the latter solvent, the compound separated in stellate groups of colourless needles, m. p. 107° (Found: C = 70·9; H = 8·6; N = 15·0. $C_{17}H_{25}ON_3$ requires C = 71·1; H = 8·7; N = 14·6 %). This substance is very sparingly soluble in light petroleum and readily soluble in methyl or ethyl alcohol, benzene, acetone, or chloroform. It is a weak base, soluble in dilute hydrochloric acid and reprecipitated by sodium acetate. All attempts to induce indole cyclisation were fruitless; the compound was recovered unchanged after boiling in concentrated hydrochloric acid solution during 15 minutes, and boiling with alcoholic zinc chloride and fusion with anhydrous zinc chloride led to no results. It is on account of these somewhat anomalous observations that we suggest an alternative to the obvious view of the constitution of the substance.

1 : 4 : 4 : 6 : 6-*Pentamethyl*-3 : 4 : 5 : 6-*tetrahydro*-5-*carboline* (VI). —When triacetonamine phenylhydrazone was heated with dilute sulphuric acid, there were strong indications of the production of an indole derivative, but the reaction proceeded more smoothly in the case of the phenylmethylhydrazone. Triacetonamine (10 gms.) and *as*-phenylmethylhydrazine (8 gms.) were mixed with acetic acid (10 c.c.), when a considerable evolution of heat occurred. The first stage of the process was completed by heating on the steam-bath during 10 minutes. Sulphuric acid (15 c.c.) diluted with water (100 c.c.) was then added and the whole heated on the steam-bath during 40 minutes. The base was isolated and dissolved in 10 per cent. hydrochloric acid. A sparingly soluble hydrochloride separated and this was collected and decomposed by aqueous sodium hydroxide with production of a crystalline base. The substance crystallised from methyl alcohol in colourless prisms and under the polarising microscope the crystals were found to be monoclinic plates having a rhombic outline. This material softened at 78° and melted at 80—86° and, after heating at 111°, the resolidified oil melted at 92—93° (Found: in air-dried material, loss at 70° = 11·0. $C_{16}H_{22}N_2,CH_4O$ requires $CH_4O$ = 11·7 %. Found: in material dried at 70°, C = 79·0; H = 9·1. $C_{16}H_{22}N_2$ requires C = 79·3; H = 9·1 %). The presence of methyl alcohol in the crystals was qualitatively proved by the formation of methyl salicylate. The substance is very readily soluble in benzene and ethyl alcohol, but may be conveniently crystallised from light petroleum. The feathery needles do not, however, exhibit a sharp melting point. Sintering occurs above 160°, and at about 170° the substance shows signs of melting and resolidifying, whilst complete clearing is observed at 180°. The colour reactions of this strong base resemble those of tetrahydro-5-carboline.

The authors wish to thank the Chemical Society for a grant from the Research Fund which has defrayed a part of the cost of this investigation.

MANCHESTER UNIVERSITY. [*Received, July 4th,* 1924.]

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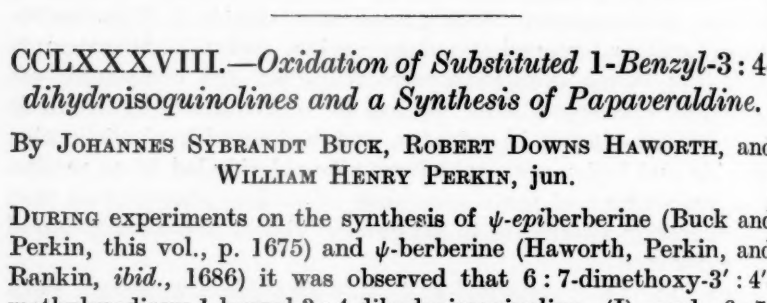
## CCLXXXVIII.—*Oxidation of Substituted* 1-*Benzyl*-3 : 4-*dihydro*isoquinolines *and a Synthesis of Papaveraldine.*

By JOHANNES SYBRANDT BUCK, ROBERT DOWNS HAWORTH, and WILLIAM HENRY PERKIN, jun.

DURING experiments on the synthesis of *ψ-epi*berberine (Buck and Perkin, this vol., p. 1675) and *ψ*-berberine (Haworth, Perkin, and Rankin, *ibid.*, 1686) it was observed that 6 : 7-dimethoxy-3′ : 4′-methylenedioxy-1-benzyl-3 : 4-dihydro*iso*quinoline (I) and 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline (II) exhibit a remarkable tendency to undergo oxidation with the formation of bases of the empirical formula $C_{19}H_{17}O_5N$.



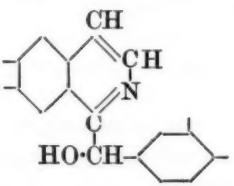

I is A with R = OMe; R′R′ = $CH_2O_2$.
II is A with RR = $CH_2O_2$; R′ = OMe.
III is B with R = OMe; R′R′ = $CH_2O_2$.
IV is B with RR = $CH_2O_2$; R′ = OMe.
VII is C with R = OMe; R′R′ = $CH_2O_2$.
VIII is C with RR = $CH_2O_2$; R′ = OMe.
IX is D with R = OMe; R′R′ = $CH_2O_2$.
X is D with RR = $CH_2O_2$; R′ = OMe.
XIV is A with R = R′ = OMe.
XV is C with R = R′ = OMe.
XVI is D with R = R′ = OMe.

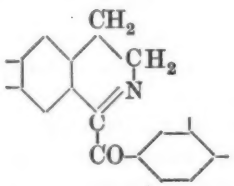
This oxidation occurs when ether, benzene, or alcoholic solutions of the substituted 1-benzyl-3 : 4-dihydro*iso*quinolines are left exposed to the air.

No change takes place when solutions in dilute acids are exposed, but oxidation can be readily effected by the addition of an alcoholic solution of iodine to the alcoholic solution of the dihydro*iso*quinoline in presence of potassium acetate. This tendency to oxidation appears to be a general property of substituted 1-benzyl-3 : 4-di-

hydro*iso*quinolines and possibly accounts for earlier experimenters describing such dihydro*iso*quinolines, which no doubt had become partly oxidised during preparation, as amorphous substances (compare Pictet and Gams, *Ber.*, 1911, **44**, 2480; Decker, Kropp, Hoyer, and Becker, *Annalen*, 1913, **395**, 299; Späth and Mosettig, *Annalen*, 1923, **433**, 139). Owing to the frequent occurrence of these products of oxidation in our own synthetical work, we thought it desirable to attempt to determine the nature of the process and the constitutions of the substances produced, and the results we have obtained are described in the present communication. The bases, $C_{19}H_{17}O_5N$, produced by the oxidation of the substituted 1-benzyl-3 : 4-dihydro*iso*quinolines, $C_{19}H_{19}O_4N$, are well-characterised, crystalline substances which yield bright yellow salts and develop a vivid green coloration when boiled with acetic anhydride. They still contain two methoxy-groups and the colour reactions with a sulphuric acid solution of phloroglucinol or of gallic acid indicate that the methylenedioxy-group is also intact. When the bases derived from (I) and (II) are reduced with tin and hydrochloric acid, they yield 6 : 7-dimethoxy-3′ : 4′-methylenedioxy-1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III; this vol., p. 1677) and 6 : 7-methylenedioxy-3 : 4-dimethoxy-1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (IV; *ibid.*, 1686), thus proving that no fundamental structural change has occurred in the molecule during the oxidation process. The two methoxy-groups and the methylenedioxy-group in the substances $C_{19}H_{17}O_5N$ account for four of the oxygen atoms and it seemed probable that the remaining oxygen must be present either as the secondary alcohol group or as the ketone group in the skeleton formulæ (V) and (VI).

(V.)




(VI.)

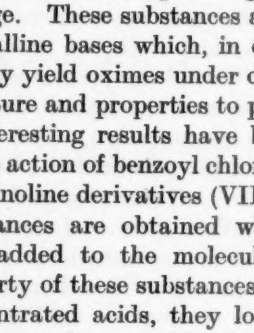
The decision between these formulæ proved to be a difficult matter and the fact that no oxime could be obtained by ordinary methods seemed to suggest that the substances $C_{19}H_{17}O_5N$ were derived from the expression (V). Ultimately, however, we were able, by employing hydroxylamine hydrochloride in pyridine solution, to obtain well-characterised oximes from both substances $C_{19}H_{17}O_5N$, and this fact, coupled with the other properties of these substances, leaves no doubt that the products of air oxidation of the bases (I) and (II) have the constitutions (VII) and (VIII).

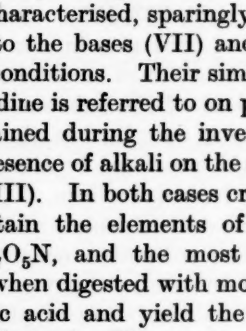
When these substances are boiled with methyl-alcoholic potassium hydroxide, further oxidation occurs with loss of two atoms of hydrogen from the dihydro*iso*quinoline rings and the *iso*quinoline derivatives (IX) and (X) are produced.

Oxidation with permanganate readily brings about the same change. These substances are well-characterised, sparingly soluble, crystalline bases which, in contrast to the bases (VII) and (VIII), readily yield oximes under ordinary conditions. Their similarity in structure and properties to papaveraldine is referred to on p. 2181.

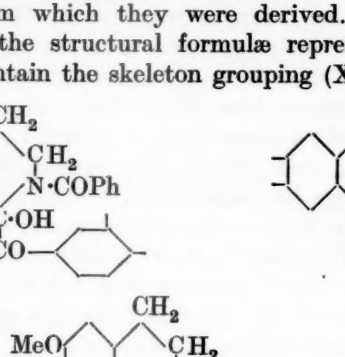
Interesting results have been obtained during the investigation of the action of benzoyl chloride in presence of alkali on the dihydro-*iso*quinoline derivatives (VII) and (VIII). In both cases crystalline substances are obtained which contain the elements of benzoic acid added to the molecule $C_{19}H_{17}O_5N$, and the most striking property of these substances is that, when digested with moderately concentrated acids, they lose benzoic acid and yield the salts of the bases from which they were derived. The most probable view is that the structural formulæ representing these benzoyl derivatives contain the skeleton grouping (XI) or (XII).

(XI.)





(XII.)



(XIII.)

Reissert (*Ber.*, 1905, **38**, 1603, 3426) has shown that quinoline reacts with benzoyl chloride in presence of sodium hydroxide to yield a benzoyl derivative of the constitution

$$CHO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NH{\cdot}COPh,$$

the pyridine ring suffering scission during the process and, on heating with dilute acids, this substance is decomposed into benzoic acid and quinoline. We incline to the view that the addition of benzoic acid to our bases $C_{19}H_{17}O_5N$ takes place in the direction indicated by Reissert's results and are of the opinion that these substances have the structure (XII). The fact that the addition of benzoic acid to the *iso*quinoline bases, $C_{19}H_{17}O_5N$, takes place so very readily is remarkable, because Reissert found (*loc. cit.*

p. 3426) that when *iso*quinoline is treated with benzoyl chloride and sodium hydroxide under the conditions employed in the case of quinoline, no addition of benzoic acid occurs.

It is pointed out on pp. 2181, 2183 that the substances (IX) and (X), produced from the substances (I) and (II) by air oxidation followed by treatment with methyl-alcoholic potassium hydroxide, are very closely related to papaveraldine (XVI), the first product of the oxidation of papaverine. If the view of the constitution of these substances put forward is correct, there seemed every probability that by varying the process a simple synthesis of papaveraldine might be achieved and this has proved to be the case. In carrying out this synthesis, 6 : 7 : 3′ : 4′-tetramethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline (XIV) was prepared by the action of phosphoryl chloride on a boiling toluene solution of homoveratroylhomoveratrylamine (XIII) and found to be identical with the base obtained by Pictet and Finkelstein (*Ber.*, 1909, **42**, 1979) in the course of their experiments on the synthesis of laudanosine.

When an alcoholic solution of this dihydro*iso*quinoline, $C_{20}H_{23}O_4N$, is exposed to the air, the base rapidly undergoes oxidation to a base $C_{20}H_{21}O_5N$ (XV), which yields bright yellow salts and develops a green coloration on boiling with acetic anhydride, properties which are exactly similar to those of the oxidised bases (VII) and (VIII) obtained from the dihydro*iso*quinolines (I) and (II) by air oxidation.

A base of the empirical formula $C_{20}H_{21}O_5N$, containing the grouping >CH·OH, and named "papaverinol," has been obtained by Stuchlik (*Monatsh.*, 1900, **21**, 814) from papaveraldine by reduction with zinc dust and acetic acid and is stated to give a green coloration with acetic anhydride and potassium acetate. We have repeated Stuchlik's reduction and are able to confirm his results with the exception that the specimen of papaverinol (m. p. 136°) we obtained did not give the green coloration with acetic anhydride and potassium acetate. The base (XV) which we obtained by the air oxidation of (XIV) melts at 190° and therefore is isomeric with papaverinol, and this fact is confirmatory evidence that the substances (VII) and (VIII) are ketones and not secondary alcohols.

When the base (XV) is digested with methyl-alcoholic potassium hydroxide or oxidised with permanganate, it is converted into a substance $C_{20}H_{19}O_5N$ (m. p. 208°) which proved to be identical with papaveraldine.

This synthesis of papaveraldine is also a synthesis of papaverine, since Goldschmiedt and Stuchlik (*Monatsh.*, 1900, **21**, 814) have shown that papaveraldine is converted into papaverine when its solution in acetic anhydride is reduced with zinc dust.

## Experimental.

6 : 7 - *Methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzoyl* - 3 : 4 - *dihydro*iso*quinoline* (VIII).—An alcoholic solution of 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-1-benzyl-3 : 4-dihydro*iso*quinoline (II; Haworth, Perkin, and Rankin, *loc. cit.*), exposed to the air in a shallow basin, gradually darkened and after some time the oxidation product began to separate. After several days it was collected and recrystallised from methyl alcohol, from which it separated in small, colourless needles, m. p. 151° (Found : C = 67·5; H = 5·2. MeO = 18·1. $C_{19}H_{17}O_5N$ requires C = 67·4; H = 5·0; MeO = 18·2 %).

This substance is readily soluble in alcohol, ether, benzene, or chloroform, but sparingly soluble in light petroleum. It dissolves in mineral acids, yielding bright yellow salts, and the solution in acetic anhydride develops a brilliant emerald green coloration on boiling.

The base dissolves in concentrated sulphuric acid to a deep orange solution and, on the addition of gallic acid, a reddish-green colour is produced which becomes brilliant green on warming. The solution in sulphuric acid containing phloroglucinol is deep red and, on warming on the steam-bath, a thick red precipitate is produced. When the base is reduced with tin and hydrochloric acid it yields 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, m. p. 84° (IV; H., P., and R., *loc. cit.*, p. 1695). The sparingly soluble *hydriodide* is precipitated when potassium iodide is added to the solution of the base in dilute hydrochloric acid and crystallises from water in long, bright yellow prisms which lose water of crystallisation at 100° and then melt at 209—211° with decomposition (Found : C = 49·0; H = 3·9. $C_{19}H_{17}O_5N$,HI requires C = 48·8; H = 3·9 %). The same hydriodide is obtained on oxidising an alcoholic solution of (II) with iodine in presence of potassium acetate and decomposing the periodide formed with sulphur dioxide. The *Oxime*. The base (0·5 gm.), dissolved in pyridine (3 c.c.), containing a little alcohol, was heated on the steam-bath for 5 minutes with hydroxylamine hydrochloride (0·2 gm.). The product was diluted with water and saturated with carbon dioxide, when the oxime separated as a crystalline powder, which was crystallised from alcohol, from which it separated in rhombic plates, m. p. 232° (decomp.) (Found : N = 8·0. $C_{19}H_{18}O_5N_2$ requires N = 7·9 %). This oxime is sparingly soluble in the usual organic solvents and slowly dissolves in dilute mineral acids to a pale yellow solution. It is soluble in sodium hydroxide and gives, in concentrated sulphuric acid, a dark orange solution which turns brown on the addition of a crystal

of potassium nitrate. The *benzoyl* derivative (XII) was obtained by dissolving the base (VIII) in excess of warm benzoyl chloride, the whole was then cooled, and the additive derivative which separated was decomposed by the addition of 10 per cent. potassium hydroxide. The supernatant liquid was decanted from the syrup, and this dissolved in a little warm alcohol, from which the benzoyl derivative separated in small, pale yellow needles, m. p. 158° (Found : C = 67·5; H = 5·1. $C_{26}H_{23}O_7N$ requires C = 67·7; H = 5·0 %). This substance is readily soluble in boiling alcohol, benzene, or chloroform, but very sparingly soluble in these solvents in the cold and is almost insoluble in ether or light petroleum. It is almost insoluble in cold dilute mineral acids, but is completely hydrolysed by boiling with 40 per cent. sulphuric acid, and, on neutralising the deep yellow solution with ammonia, the base (VIII) separates.

6 : 7-*Methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzyl*isoquinoline (X).—This substance began to separate after a few minutes when the base (VIII) (3 gms.) was heated on the steam-bath with 10 per cent. methyl-alcoholic potassium hydroxide (30 c.c.). After ½ hour, the whole was cooled, filtered, and the residue (1·7 gms.) recrystallised from much alcohol, from which it separated in glistening needles, m. p. 208° (Found : C = 67·5; H = 4·6. $C_{19}H_{15}O_5N$ requires C = 67·7; H = 4·5 %). The yield of this substance is not more than 50 per cent., and the alcoholic mother-liquors, on concentration, yield a large amount of a brown gum from which nothing crystalline could be obtained.

The substance (X) is readily soluble in boiling alcohol, benzene, acetone, or chloroform, but sparingly soluble in these solvents in the cold and also in ether or light petroleum. It dissolves in cold dilute mineral acids giving pale yellow solutions and in concentrated sulphuric acid with a brown colour. A brown coloration is also produced on boiling with acetic anhydride. The *picrate*, obtained by adding an alcoholic solution of picric acid to the alcoholic solution of the base, crystallises from methyl alcohol in small plates and melts at 206—207° with decomposition.

The *oxime* was prepared by heating the base (1 mol.), dissolved in alcohol, with a large excess of hydroxylamine hydrochloride (12 mols.) and potassium acetate (12 mols.) for 8 hours on the steam-bath. The product was filtered hot, when the oxime rapidly separated from the filtrate in hexagonal plates, m. p. 260° (decomp.) (Found : N = 8·1. $C_{19}H_{16}O_5N_2$ requires N = 7·9 %). This oxime is sparingly soluble in the usual organic solvents, but dissolves gradually in dilute acids to pale yellow solutions and is also soluble in sodium hydroxide.

6 : 7-*Dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline (VII).—This substance, obtained from 6 : 7-dimethoxy-3′ : 4′-methylenedioxy-1-benzoyl-3 : 4-dihydro*iso*quinoline (I; Buck and Perkin, *loc. cit.*) by the method described in the case of the preparation of the 6 : 7-methylenedioxy-3′ : 4′-dimethoxy-derivative (p. 2180), crystallises from alcohol in colourless, slender prisms, m. p. 151—152° (Found: C = 67·6; H = 5·1; N = 3·9; MeO = 17·6. $C_{19}H_{17}O_5N$ requires C = 67·4; H = 5·0; N = 4·1; MeO = 18·2 %). It exhibits the same colour reactions and the same behaviour towards solvents as the isomeride (VIII). It is converted, on reduction with tin and hydrochloric acid, into 6 : 7-dimethoxy-3′ : 4′-methylenedioxy-1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III; compare Buck and Perkin, *loc. cit.*, p. 1682). The *hydriodide*, obtained by the addition of potassium iodide to the solution of the base in dilute hydrochloric acid, separates as an oil which rapidly solidifies and crystallises from hot water, in which it is sparingly soluble, as a crystalline powder, m. p. 192°. The *picrate* was prepared in alcoholic solution and recrystallised from glacial acetic acid, from which it separated in yellow, glistening, rectangular plates which soften at 215° and melt at 227° with decomposition (Found: C = 52·9; H = 3·7. $C_{19}H_{17}O_5N,C_6H_3O_7N_3$ requires C = 52·8; H = 3·5 %). The *oxime*, prepared by treating the solution of the base in pyridine with hydroxylamine hydrochloride (compare p. 2180), crystallises from alcohol in colourless rhombs, m. p. 223—224° (Found: N = 7·6. $C_{19}H_{18}O_5N_2$ requires N = 7·9 %).

The *benzoyl* derivative, obtained in the same way as the benzoyl derivative of the isomeric base (VIII; p. 2181), crystallises from alcohol in pale yellow needles, m. p. 151° (Found: C = 67·7; H = 5·2. $C_{26}H_{23}O_7N$ requires C = 67·7; H = 5·0 %). When this substance is boiled with dilute sulphuric acid for 5 hours, it is hydrolysed to benzoic acid and the base (VII) from which it had been prepared.

A *monoxime* is obtained when the alcoholic solution of the benzoyl derivative is boiled with excess of hydroxylamine hydrochloride and potassium acetate. On adding sodium hydroxide and saturating with carbon dioxide, the oxime separates as an amorphous powder (Found: N = 5·7. $C_{26}H_{24}O_7N_2$ requires N = 5·9 %).

The corresponding *o-nitrobenzoyl* derivative, prepared from the base (VII) by treatment with *o*-nitrobenzoyl chloride and then with sodium hydroxide, separates from alcohol in almost colourless plates, m. p. 175—176° (Found: C = 61·4; H = 4·3. $C_{26}H_{22}O_9N_2$ requires C = 60·6; H = 4·3 %).

6 : 7-*Dimethoxy*-3′ : 4′-*methylenedioxy*-1-*benzoyl*isoquinoline (IX),

obtained (yield 60 per cent.) when the base (VII) is digested with methyl-alcoholic potassium hydroxide under the conditions described on p. 2181 in the case of the base (VIII),* separates from acetic acid in small needles, m. p. 199—200° (Found : C = 67·6; H = 4·6. $C_{19}H_{15}O_5N$ requires C = 67·7; H = 4·5 %).

The same base was obtained when the substance (VII, 1 gm.), dissolved in a little alcohol, was treated at room temperature with permanganate (0·33 gm.) dissolved in a little water. In its colour reactions and behaviour with solvents it closely resembles the isomeric substance (X). The *picrate*, prepared by the addition of a methyl-alcoholic solution of picric acid to a warm methyl-alcoholic suspension of the base, separated as a mass of bright yellow plates, m. p. 243° (Found : C = 50·3; H = 3·5. $C_{19}H_{15}O_5N,C_6H_3O_7N_3$ requires C = 50·3; H = 3·2 %).

The *oxime*, prepared from the base by the action of hydroxylamine hydrochloride and potassium acetate (compare p. 2181), crystallises from alcohol in glistening, rhombic plates, m. p. 263—264° (decomp.) (Found : N = 7·6. $C_{19}H_{16}O_5N_2$ requires N = 7·9 %).

6 : 7 : 3′ : 4′-*Tetramethoxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline* (XIV). —The homoveratroylhomoveratrylamine (XIII) required for the preparation of this substance was obtained by heating molecular proportions of 3 : 4-dimethoxyphenylacetic acid and 3 : 4-dimethoxyphenylethylamine at 200° for 2 hours (compare this vol., pp. 1680, 1694). It separated from hot alcohol in colourless crystals, melted at 124°, and proved to be identical with the substance obtained by Pictet and Finkelstein (*Ber.*, 1909, **42**, 1979). In preparing the base (XIV), homoveratroylhomoveratrylamine (30 gms.), dissolved in toluene (150 c.c.) containing phosphoryl chloride (60 c.c.), was gently boiled for 45 minutes, the product cooled and diluted with light petroleum, when a heavy dark yellow syrup separated. This was dissolved in alcohol, made alkaline with sodium hydroxide, and poured into water, when the dihydro*iso*quinoline separated as an oil, which was extracted with ether (compare P. and F., *loc. cit.*). The *picrate*, prepared in alcoholic solution, separates from a mixture of methyl alcohol and glacial acetic acid in bright yellow, prismatic needles, m. p. 168° (Found : C = 55·1; H = 4·7. $C_{20}H_{23}O_4N,C_6H_3O_7N_3$ requires C = 54·7; H = 4·6 %).

* When the alcoholic mother-liquors from this substance were poured into water, an amorphous precipitate separated, the solution of which in alcohol gradually deposited a small quantity of a crystalline substance. This substance is insoluble in dilute acids and crystallises from acetic acid in small needles, m. p. 294—296° (Found : C = 64·5; H = 5·5; N = 3·8. $C_{19}H_{17}O_6N$ requires C = 64·2; H = 4·8; N = 3·9%). It is apparently formed from the base $C_{19}H_{17}O_5N$ (VII) by the addition of an atom of oxygen, but the amount available was too small for further investigation.

6 : 7 : 3′ : 4′-*Tetramethoxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline (XV).—When the alcoholic solution of the base (XIV) was exposed to air in a shallow basin, the substance (XV) gradually separated and was purified by recrystallisation from methyl alcohol, from which it separated as a cream-coloured, glistening powder, m. p. 190—191° (Found : C = 67·6; H = 5·9. $C_{20}H_{21}O_5N$ requires C = 67·6; H = 5·9 %).

The *hydrochloride*, obtained by dissolving the base in hot 30 per cent. hydrochloric acid, separated as a mass of bright yellow crystals, m. p. 183° (decomp.) (Found : C = 59·4; H = 6·0. $C_{20}H_{21}O_5N,HCl,H_2O$ requires C = 59·9; H = 5·7 %).

The *hydriodide*, m. p. 186° (decomp.), separates as a bright orange mass of felted needles when potassium iodide is added to the warm solution of the hydrochloride. The *oxime*, prepared from the pyridine solution of the base by the action of hydroxylamine hydrochloride, crystallises from hot alcohol in colourless, hexagonal plates, m. p. 247—248° (decomp.) (Found : C = 64·9; H = 6·1; N = 7·7. $C_{20}H_{22}O_5N_2$ requires C = 64·9; H = 5·9; N = 7·6 %). It is sparingly soluble in organic solvents, but dissolves in dilute acids or alkalis. The deep orange solution in concentrated sulphuric acid becomes greenish-brown on the addition of a crystal of potassium nitrate. The *benzoyl* derivative, obtained from the base by the action of benzoyl chloride and then of sodium hydroxide (compare p. 2181), crystallises from alcohol in pale yellow needles, m. p. 160° (Found : C = 67·6; H = 5·7. $C_{27}H_{27}O_7N$ requires C = 67·9; H = 5·7 %). When this substance is boiled with dilute sulphuric acid it is hydrolysed into benzoic acid and the base (XV).

6 : 7 : 3′ : 4′-*Tetramethyoxy*-1-*benzoyl*isoquinoline (XVI)-*Papaveraldine*.—Papaveraldine was obtained (yield 65 per cent.) when the base (XV) was digested with methyl-alcoholic potassium hydroxide on the steam-bath for a few minutes. The crystalline mass which separated on cooling was recrystallised from alcohol, from which it separated in small needles, m. p. 208°. That this substance is papaveraldine was proved by a mixed melting-point determination, when there was no depression, by the preparation of the sparingly soluble hydrochloride (m. p. 209°) and of the oxime. The latter melted between 235° and 254° with frothing and darkening and, on dissolving the substance in dilute acid and precipitating with sodium carbonate, the melting point was 235°. An exactly similar behaviour was shown by the oxime of a specimen of papaveraldine prepared from papaverine.

Two of the authors (J. S. B. and R. D. H.) wish to express their gratitude to the Royal Commissioners for the Exhibition of 1851 for

Studentships which have enabled them to take part in this investigation. We are indebted to Mr. Fred Hall for the analyses given in this communication.

THE DYSON PERRINS' LABORATORY,
OXFORD.

[*Received, June 25th*, 1924.]

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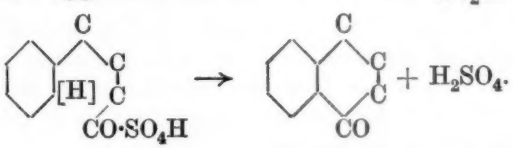
## CCLXXXIX.—*The Influence of Substituents on the Formation of Derivatives of* 1-*Hydrindone from* β-*Phenylpropionic Acids.*

By ERIC ALFRED SPEIGHT, ARNOLD STEVENSON, and JOCELYN FIELD THORPE.

A SYSTEMATIC survey has shown (Attwood, Stevenson, and Thorpe, T., 1923, **123**, 1755) that, when concentrated sulphuric acid at room temperature is employed as the condensing agent, 1-keto-tetrahydronaphthalene derivatives are obtained only from those γ-phenylbutyric acids which have a substituent in the β-position and, in addition, contain a second carboxyl group. It was suggested that this second carboxyl group led to the formation of an anhydride which added on sulphuric acid, the process being completed by the elimination of sulphuric acid, formed from the appropriate nuclear hydrogen atom.

$$(CH_2)_x\begin{<}CO\\CO\end{>}O + H_2SO_4 \rightarrow (CH_2)_x\begin{<}CO\cdot SO_4H\\CO_2H\end{.}$$

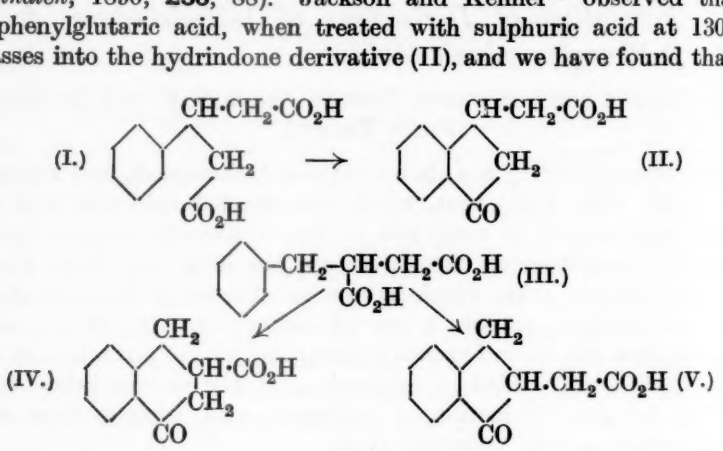



An alternative explanation put forward was that, under the catalytic influence of the sulphuric acid, the nuclear hydrogen atom migrates to the carboxyl group of the anhydride or ester. The apparent necessity for the intervention of an anhydride or ester is explained on the assumption that the migration of the hydrogen atom to the free carboxyl group is inhibited by the dynamic structure of the latter.

It was thought that further evidence bearing on the mechanism of the reaction might be obtained by investigating the influence of substituents on the formation of 1-hydrindone derivatives from β-phenylpropionic acids. Although there are but two positions into which the substituents can be introduced (instead of the three in the γ-phenylbutyric series), the range of acids available allows

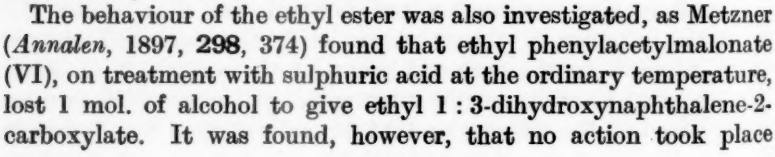
the introduction of a greater variety of substituent groups. The experiments were carried out both at room temperature and at 100°, as it was thought that this might give some indication of the relative influence of different substituents.

β-Phenylpropionic acids with the group $-CH_2 \cdot CO_2H$ as a substituent in both the α- and the β-positions are known, the former being β-phenylglutaric acid (I) (Michael, *Amer. Chem. J.*, 1887, **9**, 115) and the latter benzylsuccinic acid (III) (Fittig and Röders, *Annalen*, 1890, **256**, 88). Jackson and Kenner * observed that β-phenylglutaric acid, when treated with sulphuric acid at 130°, passes into the hydrindone derivative (II), and we have found that,




while the acid is unchanged at the ordinary temperature, ring formation takes place at 100°, the constitution of the resulting compound being proved by the formation of a semicarbazone, and the production of phthalic acid on oxidation with hot alkaline permanganate. Evidence that the anhydride is first formed is furnished by the fact that, at 100°, the anhydride of this acid gives the same hydrindone derivative.

The behaviour of the ethyl ester was also investigated, as Metzner (*Annalen*, 1897, **298**, 374) found that ethyl phenylacetylmalonate (VI), on treatment with sulphuric acid at the ordinary temperature, lost 1 mol. of alcohol to give ethyl 1 : 3-dihydroxynaphthalene-2-carboxylate. It was found, however, that no action took place

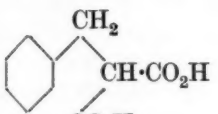



* Private communication.

at the ordinary temperature, but, at 100°, the ester was hydrolysed, giving the same acid hydrindone derivative as was obtained from β-phenylglutaric acid.

With benzylsuccinic acid (III) ring formation could take place in two ways to give, in one case, the tetrahydronaphthalene derivative (IV), and, in the other case the hydrindone derivative (V). It has already been shown (Attwood, Stevenson, and Thorpe, *loc. cit.*) that condensation takes place at room temperature and that, although absolute proof could not be obtained, there is very strong evidence in favour of the formation of the tetrahydronaphthalene derivative (IV).

Derivatives of β-phenylpropionic acid with a carboxyl group in either the α- or the β-position are available. Thus benzylmalonic acid (IX) (Conrad, *Annalen*, 1880, **204**, 174) may be regarded as α-carboxyl-β-phenylpropionic acid, and phenylsuccinic acid (X) (Rügheimer, *Ber.*, 1881, **14**, 428) as the corresponding β-derivative.



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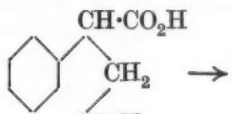
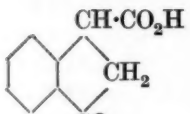


(X.)



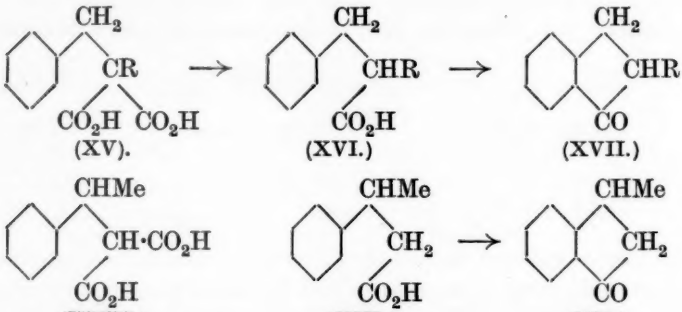
(XI.)

The former suffered deep-seated decomposition on treatment with sulphuric acid, even in the cold, whilst the latter remained unchanged at the ordinary temperature, but, at 100°, passed into the hydrindone derivative (XI), which readily gives a semicarbazone but, unlike its homologue (II), does not yield phthalic acid with hot permanganate. The oxidation can, however, be carried out by means of chromic acid.

The behaviour of ethyl benzoylmalonate (XII) (Bischoff, *Ber.*, 1883, **16**, 1044) appeared to be of interest in view of the result obtained by Metzner, to which reference has already been made. Ring formation, however, did not take place, the products being benzoic acid at 100°, and benzoylacetic acid (XIV) (Perkin, T., 1884, **45**, 170) at the ordinary temperature. The latter is the β-keto-derivative of β-phenylpropionic acid and the fact of its production by the action of sulphuric acid at the ordinary temperature shows that, under such conditions, it does not undergo ring formation, whilst, at 100°, it underwent complete decomposition. The α-keto-isomeride, phenylpyruvic acid (XIII) (Wislicenus, *Ber.*, 1887, **20**, 592), was decomposed at both temperatures.

$COPh{\cdot}CH(CO_2Et)_2$ (XII.) $CH_2Ph{\cdot}CO{\cdot}CO_2H$ (XIII.) $COPh{\cdot}CH_2{\cdot}CO_2H$ (XIV.)

A methyl group can be introduced as a substituent in either position, with or without a carboxyl group in addition, benzylmethylmalonic acid (XV; R = Me) (Conrad and Bischoff, *Annalen*, 1880, **204**, 177) and α-benzylpropionic acid (XVI; R = Me) being the α-substituted acids and phenylmethyl*iso*succinic acid (XVIII) (Kohler, *Amer. Chem. J.*, 1905, **34**, 132) and β-phenylbutyric acid (XIX) the β-substituted acids. Benzylmethylmalonic acid remained unchanged at room temperature, whilst at 100° it lost carbon dioxide and passed into the hydrindone derivative (XVII; R = Me) (Miller and Rohde, *Ber.*, 1890, **23**, 1888), which can also be obtained by the action of sulphuric acid on benzylpropionic acid at either temperature. It was also found that analogous results could be obtained when an ethyl group is substituted for the methyl group in the above acids.




Phenylmethyl*iso*succinic acid (XVIII) was completely decomposed at 100°, whilst at the ordinary temperature fission took place with formation of malonic acid. The mechanism of this somewhat unusual reaction requires further investigation.

β-Phenylbutyric acid (XIX) behaves similarly to its isomeride, giving the hydrindone derivative (XX) (Mitchell and Thorpe, T., 1910, **97**, 2275) at either temperature.

The simplest acid which could undergo the required change is β-phenylpropionic acid, but Miller and Rohde (*Ber.*, 1890, **23**, 1887) state that on treating it with sulphuric acid at 140° they obtained a small amount of a high-melting substance which was not hydrindone. We have found that, at the ordinary temperature and at 100°, ring-closure cannot be effected, but if the acid is treated with sulphuric acid for 15 minutes at 130° and rapidly cooled, 1-hydrindone itself is obtained in about 10 per cent. yield.

These reactions show that neither a second carboxyl group nor a β-substituent is necessary to bring about ring-closure. Contrasting the behaviour of corresponding pairs of substituted acetic

and malonic acids it would appear that an α-carboxyl group hinders ring-formation. Thus acetic acids of type (XVI) react at the ordinary temperature, whereas the corresponding malonic acids (XV) do not, and, at 100°, ring-formation occurs only with loss of carbon dioxide. Similarly, benzylmalonic acid (IX) is decomposed at room temperature, at 100°, and also at 130°, at which temperature β-phenylpropionic acid is converted into 1-hydrindone. On the other hand a carboxyl group in the β-position would appear to assist ring-formation, whilst an alkyl group in either position has a powerful positive effect.

## Experimental.

Unless otherwise stated, the acids required were prepared in accordance with the directions given in the literature. They were treated with from 5 to 10 times their weight of concentrated sulphuric acid and kept for 16 to 20 hours either at room temperature or at 100° on the steam-bath. The resulting mixture was then poured on to ice, any precipitate filtered off, and the filtrate extracted with ether. The precipitate and the residue from the ethereal extract were tested by the method of mixed melting points to determine if the original acid was unchanged.

1-*Ketohydrindene*-3-*acetic Acid* (II).—In the hydrolysis of the tribasic ester obtained by Michael's method (*loc. cit.*), a gum is formed which does not solidify readily. This can be avoided by hydrolysing first with alcoholic potassium hydroxide to the acid ester and then with boiling concentrated hydrochloric acid to β-phenylglutaric acid, which solidifies on cooling. Treated as above, this gave, at the ordinary temperature, a precipitate of unchanged acid; at 100°, 20 gms. of acid gave 9 gms. of precipitate, a little more being obtained from the ethereal extract. Crystallised from water, the new acid separated in glistening plates and from benzene and light petroleum in minute prisms, m. p. 154·5° [Found: 11·85 c.c;* C = 69·16; H = 5·32. $C_{11}H_{10}O_3$ (monobasic) requires 11·80 c.c.; C = 69·44; H = 5·31%]. The silver, lead, cupric, ferric, barium, and calcium salts are precipitated readily in the cold from a solution of the ammonium salt; a solution of the acid in excess of alkali when boiled or kept becomes dark red in colour, but on acidifying, the acid is reprecipitated.

The *semicarbazone* was readily prepared in alcoholic solution. It separated from alcohol as a crystalline powder darkening at 240° and melting and decomposing at 249° (Found: N = 16·98. $C_{12}H_{13}O_3N_3$ requires N = 17·00%).

The oxidation to phthalic acid was carried out in the usual

* On titration with *N*/20-sodium hydroxide.

manner (Attwood, Stevenson, and Thorpe, *loc. cit.*, p. 1764), 2·4 gms. of acid yielding 1·5 gms. of phthalic acid, which was identified by the method of mixed melting points and by titration. [Found: 18·80 c.c.* Calc. (dibasic) 18·95 c.c.]

*Ethyl β-phenylglutarate* was prepared by esterifying the acid with a 3 per cent. solution of hydrochloric acid in ethyl alcohol. It is a colourless, odourless oil, b. p. 174—175°/9 mm. (Found: C = 67·77; H = 7·55. $C_{15}H_{20}O_4$ requires C = 68·13; H = 7·64%). Treated with sulphuric acid at the ordinary temperature, it was unchanged, but at 100° gave a precipitate which was identical with the hydrindone derivative obtained from the parent acid. At 100°, the anhydride of β-phenylglutaric acid gave the same result; at the ordinary temperature, it passed to the acid.

*1-Ketohydrindene-3-carboxylic Acid* (XI).—The phenylsuccinic acid required was prepared from ethyl sodiophenylmalonate and ethyl bromoacetate in accordance with a method mentioned in a footnote by Fichter and Merchens (*Ber.*, 1901, **34**, 4175), and purified by crystallisation from water. At the ordinary temperature, the unchanged acid was precipitated, at 100°, 4 gms. of a new substance were obtained from 20 gms. of acid as a precipitate. On crystallisation from water or benzene and light petroleum, the hydrindone derivative separated in plates, m. p. 84°, which, on keeping in a vacuum, effloresced, passing to an anhydrous form, m. p. 120° [Found: 14·00 c.c.*; C = 68·40; H = 4·50. $C_{10}H_8O_3$ (monobasic) requires 13·90 c.c.; C = 68·14; H = 4·60%]. The silver, lead, cupric, ferric, barium, and calcium salts are formed readily in the cold from the ammonium salt.

The *semicarbazone* was readily formed in alcoholic solution. Crystallised from alcohol, in which it is only sparingly soluble, it darkened at about 220° and melted and decomposed at 231° (Found: N = 18·18. $C_{11}H_{11}O_3N_3$ requires N = 18·02%).

A tar resulted from the oxidation with hot alkaline permanganate in the usual manner. Oxidation was, however, effected by boiling 1 gm. for 10 minutes with 35 c.c. of a solution of 30 gms. chromic acid and 25 c.c. of concentrated sulphuric acid in 300 c.c. of water. On cooling, phthalic acid separated out and was identified by the fluorescein test and by the method of mixed melting points.

*Benzylmalonic acid* (IX) and *phenylpyruvic acid* (XIII) were decomposed by sulphuric acid, with evolution of gas, at both temperatures; there was no precipitate and the ethereal extract yielded merely a trace of dark-coloured residue which gave no semicarbazone.

*Ethyl Benzoylmalonate* (XII).—At 100°, a precipitate was obtained

* On titration with *N*/20-sodium hydroxide.

which proved to be benzoic acid; at the ordinary temperature, benzoylacetic acid was obtained and identified by its melting point and by the production of acetophenone on heating.

*Benzoylacetic Acid* (XIV).—At 100°, no precipitate was obtained and the ethereal extract yielded only a trace of brown residue which gave no semicarbazone.

1-*Keto*-2-*methylhydrindene* (XVII).—Benzylmethylmalonic acid when treated with sulphuric acid at the ordinary temperature was unchanged; at 100°, the ethereal extract gave the above compound, which was identified by conversion to its semicarbazone, m. p. 198° (Miller and Rohde, *loc. cit.*) (Found: N = 20·52. Calc., N = 20·68%). The same substance was obtained from α-benzylpropionic acid at both temperatures.

1-*Keto*-2-*ethylhydrindene* (XVII).—At the ordinary temperature, benzylethylmalonic acid (Mohr, *Chem. Zentr.*, 1905, **1**, 1597) was precipitated unchanged. The ethereal extract from 30 gms. of acid treated at 100° yielded 14 gms. of a colourless oil, with a faint, pleasant odour, b. p. 143—144°/22 mm. (Found: C = 82·34; H = 7·70. $C_{11}H_{12}O$ requires C = 82·44; H = 7·56%).

The *semicarbazone*, prepared in alcoholic solution, separates from alcohol in minute prisms melting at 202° with slight decomposition (Found: N = 19·40. $C_{12}H_{15}ON_3$ requires N = 19·34%).

The oxidation by means of chromic acid was carried out as described above, 2·1 gms. of ketone yielding 1·3 gms. of phthalic acid, which was identified as usual. The ethereal extracts from α-benzylbutyric acid (XVI) gave, at both temperatures, an oil forming a semicarbazone identical with the above.

1-*Keto*-3-*methylhydrindene* (XX).—The ethereal extracts from the treatment of β-phenylbutyric acid at both temperatures yielded an oil which gave the same semicarbazone (Found: N = 20·58. Calc., 20·68%). The melting point was 208° and not 190° as stated by Mitchell and Thorpe (*loc. cit.*).

The ethereal extract from 4 gms. of phenyl*iso*succinic acid, treated at the ordinary temperature, yielded 0·3 gms. of a solid which was proved to be malonic acid by its melting point and by titration [Found: 31·00 c.c.* Calc. (dibasic) 31·50 c.c.]. The ethereal extract from phenyl*iso*succinic acid, treated at 100°, yielded only a trace of oily residue giving no semicarbazone.

1-*Ketohydrindene*.—The ethereal extracts from the treatment of β-phenylpropionic acid at the ordinary temperature and at 100° yielded only a small amount of oily residue from which no semicarbazone could be obtained. Five grams of acid were added to 10 c.c. of concentrated sulphuric acid, previously heated to 130°,

* On titration with *N*/20-sodium hydroxide.

and the heating was continued for 15 minutes. The mixture was rapidly cooled, poured on to ice, and extracted with light petroleum, yielding 0·5 gms. of an oil which readily solidified. This was crystallised from light petroleum and identified by its melting point and by conversion to its semicarbazone.

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of the materials used in the investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, July 11th,* 1924.]

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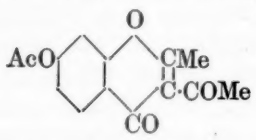
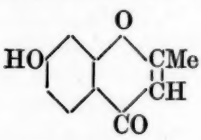
## CCXC.—*An Accessible Derivative of Chromonol.*

By JAMES ALLAN and ROBERT ROBINSON.

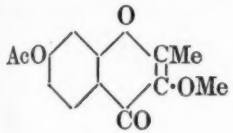
FEW applications have been made of that simple and direct synthesis of chromones which is exemplified by the preparation of 7-hydroxy-2-methylchromone (II), obtained as its diacetyl derivative (I) by strongly heating a mixture of resacetophenone, acetic anhydride, and sodium acetate (Tahara, *Ber.*, 1892, **25**, 1302; Nagai, *ibid.*, 1287; von Kostanecki and Rozycki, *Ber.*, 1901, **34**, 107).

(I.)  (II.) 

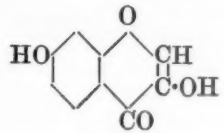
Acetylation in position 3 is not an essential feature of this reaction, and Crabtree and Robinson (J., 1918, **113**, 859) applied it to the preparation of 7-hydroxy-3-benzyl-2-methylchromone. We have now found that ω-methoxyresacetophenone (Slater and Stephen, J., 1920, **117**, 313) may be readily transformed into 3-methoxy-7-acetoxy-2-methylchromone (III) by the action of hot acetic anhydride in presence of sodium acetate. On boiling with hydriodic acid, this substance suffers hydrolysis and demethylation with formation of 3 : 7-dihydroxy-2-methylchromone, which is a homologue of the compound (IV), the product of the aerial oxidation of an alkaline solution of brazilein (Schall and Dralle, *Ber.*, 1888, **21**, 3016). Hydrolysis of the acetyl derivative (III) by means of alkali followed by methylation of the resulting phenol leads to 3 : 7-dimethoxy-2-methylchromone, and this substance reacts with magnesium phenyl bromide and magnesium anisyl bromide so as to produce the carbinol bases corresponding to pyrylium salts, which were isolated as ferrichlorides.

An extension of this chromone synthesis to the preparation of

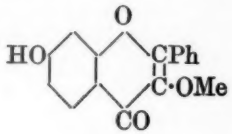
derivatives of flavone appears to be possible. When ω-methoxyresacetophenone is heated with benzoic anhydride and sodium benzoate and the product hydrolysed, 7-hydroxy-3-methoxyflavone (V) is obtained. Resacetophenone in a similar manner yields 7-hydroxyflavone, m. p. 240°, but the yield in this case is unsatisfactory and description is reserved pending further investigation of the process. It may be mentioned, however, that an intermediate product of the hydrolysis, m. p. 260°, may be isolated and this appears to be 7-hydroxy-3-benzoylflavone. The method is more generally applicable to the preparation of flavonols than of flavones and experiments on the synthesis of fisetin, datiscetin, myricetin, quercetagetin, and gossypetin along these lines have been instituted.



(III.)



(IV.)



(V.)

## EXPERIMENTAL.

7 - *Acetoxy* - 3 - *methoxy* - 2 - *methylchromone* (III).—ω-Methoxyresacetophenone (6·5 gms.), fused sodium acetate (9·8 gms.), and acetic anhydride (13 gms.) were mixed and heated (oil-bath at 170°) during 5 hours. The product was added to dilute hydrochloric acid, and the crystalline precipitate isolated (4·5 gms.). The substance crystallises from methyl alcohol in line-like needles, m. p. 113° (Found: C = 62·8; H = 5·0. $C_{13}H_{12}O_5$ requires C = 62·9; H = 4·8%).

This substance in common with the three chromone derivatives described below, dissolves in sulphuric acid to a colourless solution exhibiting bright violet fluorescence.

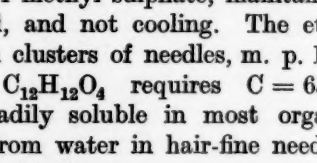
3 : 7-*Dihydroxy*-2-*methylchromone*.—Hydriodic acid (20 c.c.; *d* 1·7) was boiled under reflux with acetoxymethoxymethylchromone (1 gm.) during 45 minutes. The product precipitated by dilute sulphurous acid crystallised from methyl alcohol in clusters of colourless needles (0·4 gm.), m. p. 249° (decomp.) (Found: C = 62·2; H = 4·1. $C_{10}H_8O_4$ requires C = 62·5; H = 4·2%).

7 - *Hydroxy* - 3 - *methoxy* - 2 - *methylchromone*.—Acetoxymethoxy-methylchromone (10 gms.) was gradually dissolved when agitated with 5 per cent. aqueous sodium hydroxide (50 c.c.) and, after short heating on the steam-bath, the phenol was isolated and crystallised from methyl alcohol in prismatic needles, m. p. 214° (Found: C = 64·0; H = 5·1. $C_{11}H_{10}O_4$ requires C = 64·1; H = 4·9%), or in slender needles from much water. The colourless solution in

aqueous-alcoholic sodium hydroxide exhibits bright sky-blue fluorescence.

3 : 7-*Dimethoxy*-2-*methylchromone*.—The foregoing phenol was methylated by shaking a 5 per cent. solution in 10 per cent. aqueous sodium hydroxide with an excess of methyl sulphate, maintaining the alkaline reaction of the liquid, and not cooling. The ether crystallised from methyl alcohol in clusters of needles, m. p. 120° (Found : C = 65·6; H = 5·5. $C_{12}H_{12}O_4$ requires C = 65·5; H = 5·6%). The substance is readily soluble in most organic solvents and may be crystallised from water in hair-fine needles. The solid is not coloured in presence of iodine in aqueous suspension.

3 : 7-*Dimethoxy*-4-*phenyl*-2-*methylbenzopyrylium Ferrichloride*,




—3 : 7-Dimethoxy-2-methylchromone (0·8 gm.) dissolved in a little benzene was added to a solution of magnesium phenyl bromide (from 2·6 gms. of bromobenzene and 0·4 gm. of magnesium) in ether (50 c.c.). After several hours, the mixture was gently boiled for 10 minutes, cooled, and the product decomposed with sufficient ice to cause separation of magnesium hydroxide as a thick paste. The ether was decanted, washed with water, and then with moderately concentrated hydrochloric acid. The acid solutions were separated, combined, concentrated, and a ferrichloride precipitated by the addition of an excess of hydroferrichloric acid. The derivative crystallised from acetic acid in transparent, yellow tablets, m. p. 120° (yield 0·5 gm.) (Found : C = 44·9; H = 3·9. $C_{18}H_{17}O_3Cl_4Fe$ requires C = 45·2; H = 3·5%). The yellow solution in concentrated sulphuric acid exhibits a vivid green fluorescence.

Similarly, 3 : 7-dimethoxy-2-methylchromone and magnesium anisyl bromide yielded 3 : 7-*dimethoxy*-4-p-*methoxyphenyl*-2-*methylbenzopyrylium ferrichloride*, which crystallises from acetic acid in microscopic, pointed prisms, m. p. 114° (decomp.) (Found : C = 44·8; H = 3·8. $C_{19}H_{19}O_4Cl_4Fe$ requires C = 44·9; H = 3·7%).

7-*Hydroxy*-3-*methoxyflavone* (V).—A mixture of ω-methoxyresacetophenone (4·7 gms.), sodium benzoate (6·0 gms.), and benzoic anhydride (15·0 gms.) was heated (oil-bath at 180—185°) during 3 hours under a pressure of 20 mm. After the addition of alcohol (100 c.c.), water (10 c.c.), and potassium hydroxide (8·5 gms.), the mixture was boiled under reflux during 30 minutes, and the greater part of the alcohol then evaporated. The residue was dissolved in water, and the phenolic substance (5·5 gms.) precipitated by carbon

dioxide was crystallised from acetic acid with the aid of animal charcoal. This product contained some persistent impurity having a lower carbon content than the pure substance, which was obtained by recrystallisation from ethyl acetate in clusters of colourless needles, m. p. 227° (Found: C = 71·7; H = 4·7. $C_{16}H_{12}O_4$ requires C = 71·6; H = 4·5%).

This compound is moderately readily soluble in acetic acid and ethyl acetate and readily soluble in alcohol and acetone. Its yellow solution in concentrated sulphuric acid exhibits a weak green fluorescence.

One of us (J. A.) desires to thank the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this research.

THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1924.]

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# NOTES.

*Mononitration of* p-*Chlorotoluene.* By HERBERT HENRY HODGSON and PETER ANDERSON.

4-CHLORO-2-NITROTOLUENE (I) and 4-chloro-3-nitrotoluene (II), separately or in admixture, are converted quantitatively by sodium di- or tri-sulphide to 4-chloro-*o*-toluidine (III) and 3-amino-*p*-tolyl mercaptan (IV), respectively. A mixture of the chloronitro-compound or compounds (1 gm. in alcohol, 20 c.c.), crystallised sodium sulphide (6 gms. in water, 5 c.c.), and sulphur (1·6 gms.) is boiled under reflux for 4 hours, 100 c.c. of water are added, and the boiling is continued for 4—6 hours.

The quantities of III and IV in the reduction product are estimated: (*a*) by titration of each, after they have been separated by distillation of III with steam; (*b*) the total amine is estimated, and IV is then converted into the insoluble diazo-sulphide $C_7H_6<^{N_2}_{S}$, whilst diazotised III is coupled with β-naphthol, and the azo-compound weighed.

This process has been utilised in two directions, (1) to determine the proportions of I and II obtained by the nitration of *p*-chloro-toluene under various conditions, (2) to determine the compositions of I and II obtained from the respective nitrotoluidines by the Sandmeyer reaction.

1. *p*-Chlorotoluene (obtained in 88% yield by using 5—10 gms.

of cuprous chloride in the usual Sandmeyer reaction; compare Wynne, J., 1892, **61**, 1072, in the case of *o*-chlorotoluene) was nitrated, during a total period of 2 hours, (*a*) under Holleman's conditions (*Rec. trav. chim.*, 1909, **28**, 408), the nitric acid being added during 15, 45, and 60 minutes, respectively. The proportion of I in the product was 52·8, 58, and 58·8%, respectively (Holleman gives 58%); (*b*) with sulphuric acid (*d* 1·84; 5 parts), 10% excess of nitric acid (*d* 1·48), time of addition 1 hour. The nitration product contained I and II in the ratio 64—65/36—35, and its solidifying point was 14° (proportion of I calculated by interpolation and extrapolation from Holleman's cryoscopic data, *loc. cit.*, = 64·2 and 65·6%, respectively; (*c*) with 1 part each of nitric acid (*d* 1·5) and phosphoric oxide and 5 parts of acetic anhydride, the time of addition being as in (*b*), the ratio of I to II in the product was 50 : 50.

2. The chloronitrotoluenes I and II, prepared from the corresponding purified nitrotoluidines, gave the following results:

I, m. p. 37°. Ratio I/II = 93·9/6·2, 93·8/6·4 by analysis and 94/6 by calc.
II, s. p. 4°. " " = 6—7/94—93 by analysis and 6·6/93·4 by calc.
II, s. p. 3·5°. " " = 11—12/89—88 by analysis and 11·7/88·3 by calc. (extrap.).

The calculated values were obtained from Holleman's data on the assumption that the isomerides I and II have the same cryoscopic constant, 3·2 (II containing 6·6% of I gives $\Delta = 1{\cdot}3°$).—COLOUR CHEMISTRY DEPARTMENT, TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, June 18th*, 1924.]

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*The Photochemical Action of Iodine on Moist* p-*Chlorotoluene.* By OSWALD SILBERRAD.

WHEN *p*-chlorotoluene containing a trace of iodine is exposed to light in presence of water, toluene, *p*-chlorobenzoic acid, and 4 : 4′-dichlorodiphenylethane are produced. The formation of these compounds appears to be due to the following series of reactions:

I. $C_6H_4Cl{\cdot}CH_3 + I_2 = C_6H_4Cl{\cdot}CH_2I + HI$.
II. $2C_6H_4Cl{\cdot}CH_2I = C_6H_4Cl{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl + I_2$.
III. $C_6H_4Cl{\cdot}CH_2I + 4I + 2H_2O = C_6H_4Cl{\cdot}CO_2H + 5HI$ (compare Willgerodt, *Ber.*, 1893, **26**, 360, 361; Bamberger and Hill, *Ber.*, 1900, **33**, 535).
IV. $2HI + C_6H_4Cl{\cdot}CH_3 = C_6H_5{\cdot}CH_3 + I_2 + HCl$ (compare Klages and Lieche, *J. pr. Chem.*, 1900, [ii], **61**, 322).

A mixture of *p*-chlorotoluene (100 gms.), water (75 gms.), and iodine (0·1 gm.) exposed to sunlight for a period of 2 years, yielded, on distillation, 85·5 gms. of unaltered *p*-chlorotoluene together with the following products: Toluene 1·86 gms. (identified as benzoic acid); *p*-chlorobenzoic acid 1·35 gms. (m. p. 236°, unaltered by admixture of the pure compound); 4 : 4′-dichlorodiphenylethane 0·2 gm. (m. p. 111°, unaltered by admixture of the pure compound); free hydrogen chloride 0·82 gm. (estimated alkalimetrically and by silver).

To produce the toluene found in accordance with the suggested reactions requires 0·74 gm. of hydrogen chloride.—THE SILBERRAD RESEARCH LABORATORIES, BUCKHURST HILL, ESSEX. [*Received, August 20th,* 1924.]

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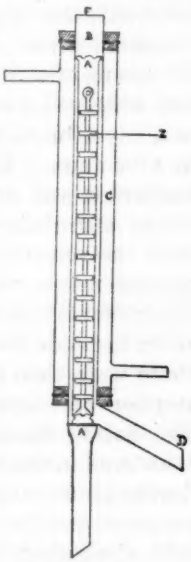
*A Combined Fractionating Column and Condenser.* By W. J. GOODERHAM.

THE combined fractionating column and condenser figured is used with an ordinary flask. The vapour from the heated liquid ascends through the middle tube, *A*, containing the fractionating surfaces, *Z*, into the outer concentric tube, *B*, which is cooled by an ordinary water jacket, *C*. The condensed vapour flows into the receiver through the tube *D*. The thermometer, held by a cork at *F*, is placed with its bulb in the top of the tube *A*. The column is easily handled and yields excellent results.




Without the discs *Z*, the apparatus acts as a condenser. It can be used as a reflux condenser by inserting the tube *D* into the distilling flask; in this case, additional cooling surface can be obtained by making direct connexion between the top of *A* and one of the entry tubes of *C*, this arrangement producing a double-surface condenser.

The apparatus can be obtained from Messrs. Townson and Mercer.—ROYAL COLLEGE OF SCIENCE, SOUTH KENSINGTON. [*Received, May 28th,* 1924.]

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# CCXCI.—*Studies with the Microbalance. Part I. The Photochemical Decomposition of Silver Bromide.*

By Ernest Johannes Hartung.

The photochemical decomposition of silver bromide has been studied gravimetrically by Volmer (*Diss.*, Leipzig, 1910), who used a delicate bending-rod balance and found that films of the halide might lose as much as 40 per cent. of the total bromine on illumination. Recently these results have been called in question by Strömberg (*Z. wiss. Phot.*, 1923, **22**, 165), who was unable to find any certain changes in weight of his films even though the microbalance employed is claimed to be capable of detecting an alteration of $10^{-8}$ mg. in its load. Koch and Schrader (*Z. Physik*, 1921, **6**, 127) have performed a large number of experiments in which silver bromide particles were suspended between the charged plates of a condenser and changes in weight on illumination were compensated by adjusting the potential on the plates. The apparatus was sensitive to 1 per cent. and only insignificant alterations in weight were detected after considerable exposure to artificial light. In a previous communication (J., 1922, **121**, 682) the author studied the problem by means of a Steele-Grant microbalance sensitive to $2 \times 10^{-5}$ mg. and obtained a maximum loss of 86 per cent. of the total halogen in a silver bromide film when illuminated under suitable conditions in a vacuum. The preliminary results have now been thoroughly confirmed and extended by improved technique with two Steele-Grant microbalances, one carrying 105 mg. and the other 43 mg.; both instruments were sensitive to $2 \times 10^{-5}$ mg. and comparative measurements with them were closely concordant. The general experimental procedure previously adopted was to prepare thin silver bromide films by brominating silvered vitreous silica supports; these were then exposed to sunlight in evacuated glass vessels, the stoppers and taps of which had been lubricated with rubber-grease. The halide films were, however, not pure and difficulty was encountered in the condensation on them of vapours from the lubricant during illumination. Very pure silver bromide films have now been prepared and the use of lubricant in the apparatus has been dispensed with altogether. A further improvement has been the adoption of flat vitreous silica sheets for carrying the photosensitive films instead of the curved supports previously used. These small sheets were drawn from rather wide, clear silica tubing and were in every way preferable to the curved ones, being more easily handled, cleaned, and protected from contamination, more easily illuminated uniformly, and less liable to chipping and breakage. The general precautions

which must be observed in handling the films have already been given.

*Preparation of Films of Pure Silver Bromide.*

It has been already shown that silver deposited chemically on glass or silica from reducing solutions contains from 1 to 3 per cent. of occluded matter, the presence of which is indicated by deficiency in the amount of bromine required to convert the film into silver bromide. It was found that regulated ignition sufficed to remove the impurity, but considerable care was necessary to prevent contamination of the hot silver film. A small electric furnace was devised for the ignition and gave complete satisfaction. A conical silica flask of 100 c.c. capacity was surrounded by the usual heating coils and packing so that only the upper portion of the neck projected from the furnace. The lid was a silica watch-glass, to the convex lower side of which was sealed a light silica rod terminating in a hook from which the film hung during the ignition. This lid was provided with a small silica handle and when in position was always completely covered with an inverted glass basin as a protection against dust. At first, glass was used instead of vitreous silica for the innermost parts of the furnace, but it was found that silver films when ignited at temperatures as low as 300° slowly but steadily gained in weight again after the initial loss due to the expulsion of the occluded matter. The greatest observed gain after an ignition of an hour was 0·0015 mg. in a film weighing 0·1304 mg. and often the increase was considerably less, although the perfect dependability of the balances left no doubt as to its reality. The origin of this source of error was not discovered, but the substitution of silica for glass removed it completely and it was then possible to ignite silvered silica films for an hour or longer at 400° without any change in weight greater than 0·0001 mg. The optimum temperature of ignition was found to be about 400°; at lower temperatures the occluded matter was slowly and incompletely driven off and at higher temperatures the risk of contaminating the film appeared to increase. At 650°, slight discrepancies were observed on subsequent bromination of the ignited films which could only be explained by diffusion of the silver into the surface of the silica sheet supporting it; in this connexion it is interesting to note that Rheinberg (*Lond. Physical Soc.*, 1920, 32) finds a temperature of 610° to 625° sufficient for platinising quartz with a permanent layer of the metal under the surface of the silica. The standard procedure finally adopted for preparing a film of pure silver bromide was as follows:—The silica support was cleaned by immersion in pure concentrated nitric acid, washed in distilled water, and dried by gentle ignition over a small alcohol flame. After being weighed,

it was silvered in the well-known Rochelle-salt silvering solution, soaked in repeated changes of distilled water, and dried over pure concentrated sulphuric acid in an evacuated desiccator. Filtered purified air was then admitted and the film weighed. Two ignitions of 30 minutes' duration at 400° followed, the new weight being then perfectly constant. Exposure to carefully purified bromine vapour resulted in the formation of a uniform opalescent film of the halide. The speed of bromination of the matt white silver was markedly less than that of a brilliant film before ignition, but in 30 minutes practically the whole of the halogen had been added and subsequent exposure to bromine vapour for a few minutes completed the addition with only insignificant increase in weight. A series of tests is summarised in Table I, in which is also included the loss in weight occasioned by dissolving the bromide film from the silica with a concentrated solution of sodium thiosulphate. The weights are all given in milligrams.

TABLE I.

| Wt. of silver from solution. | Wt. of silver after ignition. | Percentage loss in wt. | Wt. of film after bromination. | Loss after thiosulphate treatment. | Theoretical wt. of silver bromide. |
|---|---|---|---|---|---|
| 0·2133 | 0·2102 | 1·45 | 0·3658 | 0·3656 | 0·3659 |
| 0·1440 | 0·1429 | 0·76 | 0·2489 | — | 0·2488 |
| 0·1211 | 0·1195 | 1·32 | 0·2080 | 0·2078 | 0·2080 |
| 0·0493 | 0·0488 | 1·01 | 0·0848 | — | 0·0850 |
| 0·0954 | 0·0946 | 0·84 | 0·1651 | 0·1649 | 0·1647 |

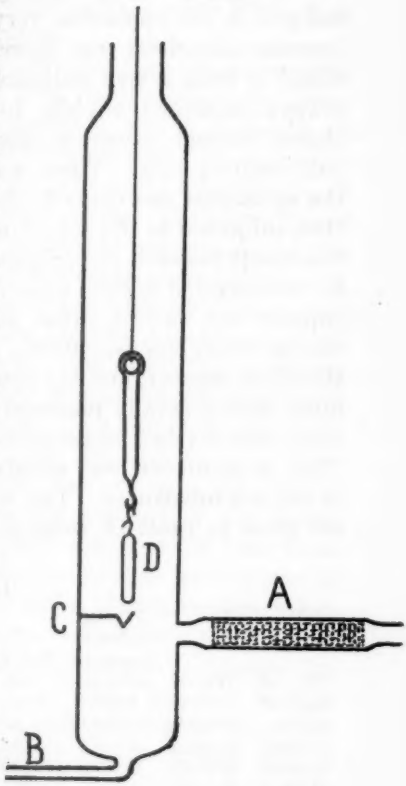
It will be noted that there is good agreement between the observed weight of silver bromide and that in the last column calculated from the weight of ignited silver in each case. The maximum divergence is 1 part in 400 and the average is 1 part in 1600. In numerous subsequent experiments, the maximum divergence was not greater than 1 part in 1000 and the average was less than 1 part in 2400. There was no evidence of any formation of perbromides.

*Photochemical Decomposition of Silver Bromide in a Vacuum.*

It has already been shown that thin films of silver bromide lose weight slowly when insolated in air and that the decomposition is much more rapid in a vacuum. In the earlier experiments, evidence was obtained that the vapours from the lubricant on the stopper and stopcocks of the exposing vessel condensed on the photosensitive films to some extent during exposure. In addition to affecting the weights of the preparations, such condensation interfered with the free escape of the halogen from the illuminated surfaces. An apparatus was therefore devised in which the films could be sealed with the blowpipe without damaging them in any way. This

obviated the use of rubber grease altogether and the experiments were in consequence much more trustworthy. The exposing vessel (Fig. 1) is a thin glass tube, about 25 cm. long and 3·5 cm. in diameter, narrowed at the upper end to permit of convenient sealing and provided with two tubules, A and B. Tube A contains a roll of clean metal, usually copper gauze, to act as bromine absorbent and is finally sealed to the pump to exhaust the apparatus. Tube B is used to convey a stream of purified filtered air into the vessel during the sealing operations. As A is closed at this time, the current of air passes out at the upper end of the apparatus and effectually protects the silver bromide film hanging on the slender glass hook, C, from contamination by the blowpipe gases. This protection is extremely important, because hot flame gases rapidly attack silver and its halogen salts. B is provided with a terminal capillary which is subsequently used, after exposure is complete, to admit purified air into the evacuated apparatus in a gentle stream. The film D is lowered into the vessel on a weighted glass hook hanging from a waxed linen thread and withdrawal of the insolated film is accomplished in the same manner at the conclusion of the exposure.

FIG. 1.




A mercury pump was used for the evacuation, which was carried on at intervals through purified phosphorus pentoxide until the pressure of the permanent gases had fallen below 0·001 mm. As heating of the vessel was inadmissible owing to the sensitive nature of the silver bromide film, adsorbed gases and moisture could not be driven from the glass, and mercury vapour also must have been present. The total quantity of the last could never have exceeded 0·0015 mg. in any experiment and silver bromide was shown to be unaffected by it. The most efficient bromine absorbent used was copper gauze; metallic zinc was much inferior, as were also solid sodium hydroxide and magnesium. After sealing from the pump,

the apparatus was exposed on the roof of the laboratory for a definite period. The incident radiation varied from brilliant sunshine to dull diffused light, but no measures of the variable intensity were made because the colour, opacity, and reflecting power of the photosensitive films varied continuously and made any estimate of the amount of radiant energy photochemically absorbed by them quite impossible. It was hoped to prevent the attainment of photochemical equilibrium, and so to make the decomposition of the silver bromide complete, by keeping the partial pressure of the liberated halogen in the apparatus very low. The side tube containing the bromine absorbent was therefore wrapped in opaque material to shield it from active radiation. The originally pearly-yellow film always darkened rapidly to dusky violet on exposure, passing thence through bronze-purple to brown, and eventually becoming pale ochre-yellow. When no further change could be detected, the apparatus was opened, the film removed and weighed. It was then subjected to the action of bromine vapour and reweighed; this treatment restored the original appearance of the film. Immersion in concentrated sodium thiosulphate solution followed and the silica support was washed, dried, and finally weighed. This final weight was generally less than 0·0005 mg. in excess of the original weight of the silica support, and the usual cleaning process with concentrated nitric acid generally rendered the two identical. As an interval of three months had sometimes elapsed between the two weighings, their concordance was satisfactory evidence of the dependability of the microbalances. The summarised results of the experiments are given in Table II, weights being recorded in milligrams.

TABLE II.

| Wt. of ignited silver. | Wt. of silver bromide. | Wt. of silver bromide calculated from silver. | Wt. of film after exposure. | Wt. after rebromination. | Wt. removed by thiosulphate. | Percentage of total bromine lost. | Days of exposure. | Bromine absorbent. |
|---|---|---|---|---|---|---|---|---|
| 0·0943 | 0·1643 | 0·1642 | 0·1171 | 0·1654 | 0·1647 | 67·4 | 13 | Mg |
| 0·1085 | 0·1889 | 0·1890 | 0·1131 | 0·1899 | 0·1894 | 94·3 | 63 | Mg |
| 0·1852 | 0·3221 | 0·3224 | 0·2355 | 0·3231 | 0·3228 | 63·3 | 10 | NaOH |
| 0·1511 | 0·2632 | 0·2631 | 0·1551 | 0·2637 | 0·2634 | 96·4 | 63 | NaOH |
| 0·0706 | 0·1229 | 0·1229 | 0·0731 | 0·1229 | 0·1227 | 95·2 | 6 | Cu |
| 0·1718 | 0·2994 | 0·2991 | 0·1761 | 0·3005 | 0·2998 | 96·6 | 13 | Cu |
| 0·1645 | 0·2863 | 0·2863 | 0·1729 | 0·2874 | 0·2868 | 93·1 | 50 | Cu |

It is evident from the periods of exposure given in the penultimate column that decomposition of the silver bromide took place most rapidly in the presence of copper, which was always heavily tarnished by the liberated bromine. When magnesium was used as absorbent, no visible alteration of the metal occurred and subsequent testing

showed that no trace of bromine had combined with it, the major portion being held on the glass walls of the apparatus, from which it could be washed as soluble bromide by dilute nitric acid. The same behaviour was noticed with sodium hydroxide as absorbent, although, as the solid contained some halogen salt originally, it could not be proved that no bromine had been absorbed by it. The adsorption of the halogen by the glass was evidently very slow, which explains why prolonged irradiation was necessary to obtain extensive decomposition. In the presence of copper, only a small fraction of the evolved bromine was held by the glass.

The results of the experiments show that the photochemical decomposition of silver bromide has been made almost complete. Repeated attempts to remove the remaining 4 or 5 per cent. of bromine by prolonged insolation were unsuccessful. It is possible that this residual halogen is tenaciously held as an adsorbed layer on the surface of the silver formed by irradiation. That this surface is very extensive is shown by the pulverulent appearance of the exposed film and by the very rapid formation of silver bromide on bromination when compared with the speed with which a simple ignited silver film is attacked. It is also possible, however, that all the bromine has escaped and that the resulting silver has been contaminated by gases arising from the glass walls of the exposing vessel or by the atmosphere prior to weighing. The results obtained by rebrominating the films favour this view, because in every case except one the new film has been slightly heavier than the original silver bromide. This applies also to the amount of the halide removed by solution in sodium thiosulphate and it is felt that these differences cannot possibly be accounted for by such gross errors as accumulation of dust or other contamination during manipulation. Experiments on the rate of bromination of silver films showed that when addition of halogen to an exposed film took place in stages, the final weight of the film was sometimes more than 5 per cent. heavier than the original film before insolation. Usually the whole of the material on the silica could be removed by treatment with sodium thiosulphate solution. Simple ignited silver films did not show such anomalous behaviour after progressive bromination. The origin of these discrepancies has not been traced with certainty, but oxidation is probably partly responsible, because insolated silver bromide films slowly gain in weight when preserved in dry carbon dioxide-free air. It will not be possible to decide the question definitely until an accurate estimation of the very small amounts of bromine presumably remaining in the insolated films of silver bromide can be made.

*Rate of Bromination of Silver Films.*

It has not been possible to study either the rate of decomposition of silver bromide or the attainment of photochemical equilibrium under constant high intensity irradiation, owing to the continual progressive variation in reflectivity, opacity, and colour of the films and to the very small equilibrium pressures of the halogen. Although the formation of silver bromide from its elements in darkness may not follow the same course as the decomposition in light, yet experiments on the rate of bromination of silver are of interest, more especially as it has been claimed by Baur and others that a change in the speed of reaction takes place when approximately half of the halogen has been added. This has been adduced recently by Plotnikov ("Photochemie," p. 339) as evidence for the formation of silver sub-bromide. The rate of bromination of silver was therefore determined by subjecting ignited silver films to progressive attack by bromine vapour of known constant concentration until the normal bromide was completely formed. The apparatus was a large glass bottle of 3·5 litres capacity, into the narrow neck of which either of two ground glass stoppers fitted accurately. To the base of one stopper a glass rod terminating in a hook was cemented; this served to suspend the silver film during the experiment. Bromine vapour was distilled into the bottle, which was then closed and immersed in a thermostat at 25° (regulated to 0·1°) so that only the neck projected. The film was introduced for definite times by changing the stoppers rapidly and, owing to the capacity of the bottle, the loss of bromine during these repeated operations was insignificant. After each immersion in the bromine vapour the film was weighed. Some experiments were also performed with insolated bromide films which had lost the major portion of the halogen. At the conclusion of each run, the bromine in the bottle was estimated volumetrically in the usual way with potassium iodide and sodium thiosulphate. The results are given in Tables III to VII, the first column showing the weight of the film in mg., the second the halogen absorbed as percentage of that necessary to form pure silver bromide, and the third column the total time of bromination in seconds. The bracketed numbers in Tables VI and VII denote the amounts of halogen in the insolated films at the beginning of the series. In every case the total area of the film was 146 sq. mm.

These results are shown graphically in Fig. 2. It is evident that the insolated films (curves 4 and 5 in the figure) are attacked by the bromine much more rapidly than the simple ignited silver films and that secondary influences have operated to render the absorbed halogen apparently in excess of that required to form the simple

TABLE III (Curve 1).

Conc. of Br 1·252 mg.-atoms per litre.

| Wt. of film. | % of total Br. | Time (secs.). |
|---|---|---|
| 0·0694 | — | — |
| 0·0767 | 14·2 | 5 |
| 0·0828 | 26·1 | 15 |
| 0·0863 | 32·9 | 30 |
| 0·0899 | 39·9 | 60 |
| 0·0947 | 49·2 | 120 |
| 0·0988 | 57·2 | 180 |
| 0·1030 | 65·4 | 240 |
| 0·1100 | 79·0 | 300 |
| 0·1135 | 85·8 | 360 |
| 0·1164 | 91·4 | 420 |
| 0·1182 | 94·9 | 480 |
| 0·1208 | 100·0 | 660 |

TABLE IV (Curve 2).

Conc. of Br 1·105 mg.-atoms per litre.

| Wt. of film. | % of total Br. | Time (secs.). |
|---|---|---|
| 0·0916 | — | — |
| 0·0999 | 12·2 | 6 |
| 0·1054 | 20·3 | 15 |
| 0·1096 | 26·5 | 30 |
| 0·1136 | 32·4 | 60 |
| 0·1189 | 40·2 | 120 |
| 0·1237 | 47·3 | 180 |
| 0·1283 | 54·0 | 240 |
| 0·1343 | 62·9 | 320 |
| 0·1403 | 71·7 | 400 |
| 0·1465 | 80·8 | 480 |
| 0·1521 | 89·1 | 560 |
| 0·1568 | 96·0 | 640 |
| 0·1598 | 100·4 | 820 |

TABLE V (Curve 3).

Conc. of Br 0·619 mg.-atoms per litre.

| Wt. of film. | % of total Br. | Time (secs.). |
|---|---|---|
| 0·0962 | — | — |
| 0·1020 | 8·1 | 5 |
| 0·1062 | 14·0 | 15 |
| 0·1105 | 20·1 | 30 |
| 0·1147 | 26·0 | 60 |
| 0·1197 | 33·0 | 120 |
| 0·1248 | 40·1 | 210 |
| 0·1292 | 46·3 | 300 |
| 0·1338 | 52·7 | 390 |
| 0·1413 | 63·3 | 540 |
| 0·1487 | 73·6 | 720 |
| 0·1559 | 83·7 | 900 |
| 0·1610 | 90·9 | 1080 |

TABLE VI (Curve 4).

Conc. of Br 1·050 mg.-atoms per litre.

| Wt. of film. | % of total Br. | Time (secs.). |
|---|---|---|
| 0·1708 | (10·0) | — |
| 0·2077 | 41·5 | 5 |
| 0·2142 | 47·0 | 10 |
| 0·2202 | 52·1 | 20 |
| 0·2277 | 58·5 | 40 |
| 0·2389 | 68·0 | 80 |
| 0·2475 | 75·3 | 120 |
| 0·2587 | 84·8 | 180 |
| 0·2658 | 90·8 | 240 |
| 0·2714 | 95·6 | 300 |
| 0·2849 | 107·0 | — |

TABLE VII (Curve 5).

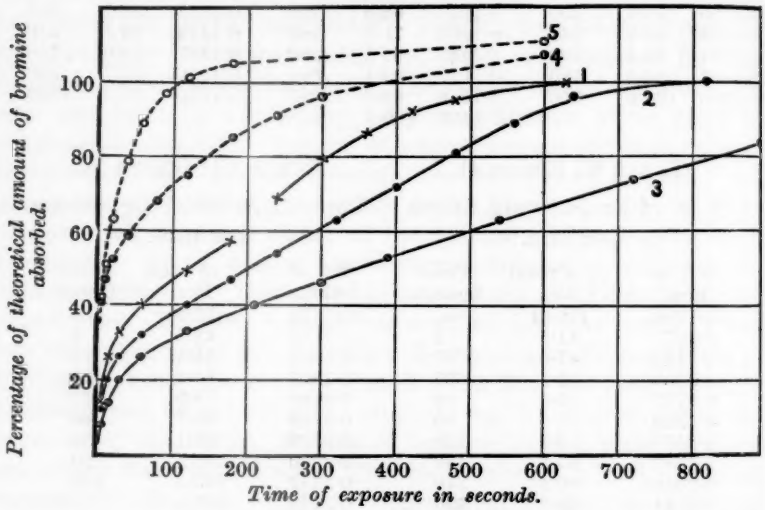
Conc. of Br 0·525 mg.-atoms per litre.

| Wt. of film. | % of total Br. | Time (secs.). |
|---|---|---|
| 0·1512 | (17·7) | — |
| 0·1756 | 42·3 | 5 |
| 0·1846 | 51·4 | 10 |
| 0·1965 | 63·4 | 20 |
| 0·2118 | 78·9 | 40 |
| 0·2215 | 88·7 | 60 |
| 0·2298 | 97·1 | 90 |
| 0·2340 | 101·3 | 120 |
| 0·2382 | 105·5 | 180 |
| 0·2440 | 111·4 | — |

halide. The colour changes on bromination were, however, very similar in both cases and closely followed in inverse order those observed when pure silver bromide films were insolated in the usual way. The greater speed of bromination of previously irradiated films is probably due to increased surface; indeed, it is probable that removal of bromine atoms from the space lattice of silver bromide by photochemical action results in the formation of a porous open structure of silver atoms and it is to be expected that such a structure would be attacked by the halogen much more readily than a consolidated crystalline film of ignited silver. The speed of reaction evidently increases rapidly with increasing concentration of bromine vapour, but, although the general shapes of the curves are similar, it has not been possible to express them by any general equation. It is probable that the reaction is influenced by secondary effects

such as temperature changes at the surface of the film, adsorbed gas layers, and other complications. There is, however, no evidence of any irregularities which might indicate the transient formation of sub-bromides in the film. The discontinuity in curve 1 is due to an interruption in the series of exposures to the bromine vapour for 36 hours. During this interval, the film was kept in dry air and some change, possibly oxidation, took place with the result that a new curve was obtained on completing the progressive addition of the halogen. Arguments against the existence of silver sub-haloids have been well summarised by Reinders (*Z. physikal. Chem.*, 1911,

FIG. 2.




**77**, 356) and Bancroft (*Trans. Faraday Soc.*, 1923, **19**, 250). The conclusions reached by these investigators are borne out by the present work, in which it has been shown definitely that pure silver bromide decomposes into silver and bromine on illumination. There is also no reason to suppose that the production of the latent image when silver halides are illuminated for very short periods is not due to incipient decomposition of the same type. The most generally accepted view at present is that the latent image consists of silver adsorbed on the surface of the yet unchanged halide, and Bancroft ascribes the action of developers to differential adsorption on the film which is conditioned by the presence of this silver layer.

*Summary.*

1. The photochemical decomposition of silver bromide has been investigated by means of the microbalance.

2. The preparation and testing of films of very pure silver bromide is described.

3. An improved apparatus is described in which sensitive films may be sealed without injury.

4. It is shown that more than 96 per cent. of the bromine may be expelled by insolating thin films of silver bromide in a vacuum in the presence of a suitable halogen absorbent.

5. The rate of bromination of thin silver films has been investigated and no evidence of the formation of silver sub-bromides has been obtained.

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## CCXCII.—*The Polysulphides of the Alkali Metals. Part V. The Monosulphide and Disulphide of Lithium.*

By JOHN SMEATH THOMAS and JOHN HENRY JONES.

VERY little is known of the sulphur compounds of lithium. Reference may be made to the work of Berzelius (*Pogg. Ann.*, 1826, **6**, 439), who, by the evaporation of an aqueous solution containing lithium hydrosulphide, obtained a syrup to which he gave the formula $Li_2S_2,nH_2O$. Vauquelin (*Ann. Chim. Phys.*, 1918, [ii], **7**, 284), by fusing lithium hydroxide with sulphur, obtained a substance which he considered to be a polysulphide. Troost (*ibid.*, 1857, [iii], **51**, 128), prepared an amorphous substance, which he regarded as lithium monosulphide, by the action of sulphur vapour on lithium metal, and also by reducing the sulphate with carbon. Mourlot (*ibid.*, 1899, [vii], **17**, 513), by the same method but at the temperature of the electric furnace, claims to have prepared monosulphide crystals with a specific gravity of 1·63. The products described by the two last-mentioned authors were yellow in colour, and therefore were probably largely contaminated with polysulphide (see Thomas and Rule, J., 1913, **103**, 871).

In the present investigation attempts were first made to convert lithium hydrosulphide into the monosulphide by the method of Thomas and Rule (*loc. cit.*). Lithium hydrosulphide, in the form of

the alcoholate $2LiHS,C_2H_5{\cdot}OH$ (Jones and Thomas, J., 1923, **123**, 3285), was heated in a vacuum in presence of absorbents for hydrogen sulphide and alcohol. Since, however, lithium hydrosulphide is able to absorb alcohol, even in presence of phosphoric oxide (see Jones and Thomas, *loc. cit.*), the preparation of anhydrous lithium hydrosulphide from the alcoholate was found to be impossible. In every attempt to eliminate hydrogen sulphide the loss of weight was approximately the same; it was greater than could be accounted for by loss of either hydrogen sulphide or alcohol alone, but less than would be required by the complete elimination of both. This indicates a partial alcoholysis of the compound, the two reactions $2LiHS \longrightarrow Li_2S + H_2S$ and $LiHS + C_2H_5{\cdot}OH \longrightarrow C_2H_5{\cdot}OLi + H_2S$ proceeding simultaneously (compare the alcoholysis of sodium tetrasulphide, Thomas and Rule, J., 1917, **111**, 1083).

When the alcoholate of lithium hydrosulphide was very rapidly heated to 360° in an evacuated vessel, a faintly yellowish-brown product, containing approximately 55·6 per cent. of the monosulphide, was obtained: the remainder was lithium ethoxide. On passing hydrogen with about 10 per cent. of hydrogen sulphide over the material at 120°, the ethoxide was reconverted into hydrosulphide and alcohol distilled over. When the mass was then heated to 360° in presence of phosphoric oxide and solid potassium hydroxide, nearly pure monosulphide was produced. It contained a very small quantity of polysulphide, to which, in the authors' opinion, the substance owed its faintly brown colour. By the use of anhydrous hydrosulphide the formation of this trace of polysulphide would probably be avoided and the highly pure monosulphide could thus be obtained.

Lithium hydrosulphide reacts with sulphur in the same way as the other alkali hydrosulphides, and the methods previously used for the preparation of the polysulphides are applicable, therefore, in the case of lithium also. Non-aqueous solvents, successfully applied in preparing the polysulphides of sodium, potassium, and ammonium (Rule and Thomas, J., 1914, **105**, 177), are particularly necessary in the case of lithium, for owing to its lower electropositivity the compounds of this metal are more liable to hydrolysis.

The only lithium polysulphide obtained was the disulphide, and even this compound could not be obtained free from alcohol. Solutions of lithium hydrosulphide in alcohol take up more sulphur than can be dissolved in corresponding solutions of any of the other alkali metals, and, indeed, this property appears to diminish regularly with increasing atomic weight of the metal. The stable lithium polysulphide, however, which can be separated from these solutions contains a smaller number of sulphur atoms in the molecule

than does the polysulphide of any other alkali metal prepared in a similar way. In every case, the disulphide is the most stable compound, and the number of additional sulphur atoms taken up beyond that stage seems to depend on the electropositivity of the metal. As the atomic weight of the metal increases, the stability of the polysulphides becomes greater, and the structure of the compounds obtained becomes more complex. Thus, lithium yields a disulphide, sodium a tetrasulphide, potassium and ammonium form pentasulphides, whilst hexasulphides of rubidium and cæsium have been described. The stability relationships of the polyhalides of the alkali metals may be recalled in this connexion.

The solubility of the polysulphides in alcohol varies inversely as the stability. Owing to their comparative insolubility the isolation of the polysulphides of the more electropositive elements presents no serious difficulty. With lithium, however, crystallisation from alcohol was impossible, precipitation with ether unsatisfactory, and other methods of separation had to be employed. These methods left some doubt as to the real nature of the final product. When, however, it was treated with allyl iodide, diallyl disulphide was obtained, and hence the compound has a composition similar to that of the disulphides of sodium and potassium (compare Thomas and Riding, following paper).

Lithium disulphide differs from these two substances in its behaviour towards nitrobenzene and pyridine. With nitrobenzene, no colour change was observed, but the addition of a small quantity of the disulphide to pyridine gave immediately a bluish-green coloration which gradually darkened until finally the liquid had a deep olive-green tint. This colour is probably due to the formation of an unstable additive compound (compare Thomas and Riding, J., 1923, **123**, 3274). The tendency towards the formation of such compounds appears to be less in the case of lithium than that shown by the polysulphides of ammonium, potassium, and sodium. Filter-paper is coloured brown by this liquid.

## Experimental.

In the analysis of the products obtained, lithium was estimated by direct titration with $N/10$-sulphuric acid. The total sulphur was determined by treating a weighed quantity of the substance with a 10 per cent. solution of sodium hydroxide, oxidising the sulphur with bromine, and precipitating the sulphate as barium sulphate. The sulphur convertible into hydrogen sulphide was estimated by slowly adding a solution of the substance in much water to $N/10$-iodine, acidified with hydrochloric acid, and titrating the excess of iodine with $N/10$-sodium thiosulphate. In the case of the

disulphide, the polysulphide sulphur was also estimated, by Küster and Heberlein's method.

*Conversion of Lithium Hydrosulphide into the Monosulphide.*—In an attempt to prepare the anhydrous hydrosulphide from the alcoholate (Jones and Thomas, J., 1923, **123**, 3290), 0·2644 gm. of the latter was heated at 70° in a vacuum and in presence of phosphoric oxide, to constant weight. The substance became faintly yellow and the loss in weight was 33·86% (for complete removal of alcohol, loss = 36·5%). The product contained Li 16·71, S 30·67% (LiHS requires Li = 17·35; S = 80·15%). Evidently the loss in weight was due to elimination of both alcohol and hydrogen sulphide. Complete alcoholysis in accordance with the equation $2LiSH,EtOH \longrightarrow LiSH + EtOLi + H_2S$ would occasion a loss in weight of 27% and the product should contain 15·23% Li and 35·89% S. It would appear, therefore, that not only is the removal of alcohol incomplete, but that a certain amount of the anhydrous hydrosulphide formed loses hydrogen sulphide with the formation of the monosulphide. Further experiments made it clear that this is actually the case.

When the temperature was increased to 200°, a further small quantity of alcohol was expelled. In view of the experiments of Thomas and Rule (*loc. cit.*) on the formation of sodium monosulphide, it seemed highly improbable that pure lithium monosulphide would result from the interaction of the products of alcoholysis in accordance with the equation $LiSH + EtOLi \longrightarrow Li_2S + EtOH$.

The effect of rapidly heating the alcoholate in a vacuum to a much higher temperature was thereupon tried. A hard glass tube (fitted with side tubes containing phosphoric oxide and potassium hydroxide) containing 0·7122 gm. of the substance was evacuated and plunged into a bath at 360°. A vigorous evolution of gas immediately occurred and alcohol condensed in the cool parts of the apparatus; after 3 hours, no further loss in weight could be observed, even at 400° (loss = 49·03%).

The product (Found: Li = 22·54; S = 38·79%) was slightly yellow, dissolved completely in water, and, on treatment with dilute acid, only a faint turbidity was produced. Apart from the trace of polysulphide thereby indicated, the product must have consisted entirely of monosulphide and ethoxide, and a simple calculation, based on the foregoing figures, gives the proportions as $Li_2S$ 55·59, LiOEt 43·03 per cent. The formation of these substances in the ratio given would necessitate a loss in weight of 51·36 per cent.

0·6197 Gram of the alcoholate was converted into a mixture of lithium ethoxide and monosulphide by heating the substance in a vacuum, in the manner already described, at 120° for 2 hours (loss = 47·3%, so that some unchanged hydrosulphide probably also

remained). A fairly rapid stream of dry hydrogen containing 10 per cent. of hydrogen sulphide was then passed over the faintly yellow mass for about 3 hours, alcohol being expelled, and the substance, after cooling, was rapidly transferred to the tube employed in the previous experiment. This tube, after the apparatus had been evacuated, was then plunged into the bath at 360°, and was allowed to remain therein for 3 hours, the hydrogen sulphide evolved being continuously removed by suction. No condensation of alcohol was observed (Found: loss = 63·68. Loss, calculated on the basis of complete conversion into monosulphide, = 63·51%. Found: in the product, Li = 29·71; S = 69·47. $Li_2S$ requires Li = 30·24; S = 69·76%). This nearly pure lithium monosulphide had a buff tint rather darker than that of sodium monosulphide. Its aqueous solution developed a faint turbidity on acidification with hydrochloric acid, hydrogen sulphide being evolved, but the amount of polysulphide present was too small to be estimated. The monosulphide appears to be less soluble than the hydrosulphide in alcohol, and the solution dissolves sulphur less readily than in that case; the evolution of hydrogen sulphide during the dissolution is probably due to alcoholysis, whereby a certain amount of hydrosulphide would be produced, for whereas alcoholic solutions of the hydrosulphides of the more electro-positive alkali metals dissolve sulphur readily, with the evolution of hydrogen sulphide and the formation of polysulphides, the monosulphides only dissolve sulphur with some difficulty and to a much more limited extent.

*The Solubility of Sulphur in Alcoholic Solutions of Lithium Hydrosulphide.*—Three determinations were made, at 80°, 25°, and 15°, the lithium hydrosulphide solution being in each case 0·501*N*. A solution of the hydrosulphide (*ca.* 0·5*N*), through which a current of dry hydrogen was passing, was boiled under reflux with excess of sulphur for 2 hours. From the weight of lithium found in a sample of the clear liquid after settling, the exact strength of the original hydrosulphide solution was calculated. In this way the solubility was determined at the temperature of the boiling solution.

The remainder of the solution, together with the sulphur, was divided into two parts. Each portion was placed in a well-stoppered bottle from which all air was removed and was then kept in a thermostat at the required temperature for several days before analysis.

The results obtained (for 0·501*N*-lithium hydrosulphide: ratio metal: sulphur = 2 : 7·99 at 80°, 2 : 6·94 at 25°, 2 : 6·52 at 15°) are in good general agreement with the tendency observed in the case of the other hydrosulphides (Thomas and Riding, J., 1923, 123, 1733). Comparing the values obtained at 25° with one

another, it will be seen that there is a steady diminution in the number of atoms of sulphur associated with two atoms of the metal as the atomic weight of the metal increases. The fact that more sulphur is present in these solutions than is required for the formation of the highest stable polysulphide is probably to be accounted for by the residual affinity of the polysulphide molecule. Lithium, being the least electro-positive of this group of elements, possesses the greatest residual valency, and thus in the case of this element the largest quantity of sulphur will be required to form the full valency complex.

*Lithium Disulphide.*—An alcoholic solution of lithium hydrosulphide (prepared from 5 gms. of anhydrous lithium chloride; Jones and Thomas, *loc. cit.*) was boiled with excess of sulphur under reflux for about an hour in a current of dry hydrogen. Hydrogen sulphide was rapidly evolved and the solution became dark red, although not to the same extent as in the case of the corresponding compounds of sodium, potassium, and ammonium. A small amount of sulphur remained undissolved. No separation of polysulphide took place on cooling, but crystals of sulphur were deposited. After filtration, the solution was concentrated in a current of hydrogen to a volume of about 25 c.c.; on cooling, more sulphur was deposited, but no polysulphide. On further concentration, the liquid set, on cooling, to a jelly, but in no case did crystallisation of polysulphide take place. When, by repeated concentration in the manner indicated, the most complete separation of sulphur possible without loss of polysulphide had been effected, the clear solution was again concentrated in a current of hydrogen. The greenish-yellow jelly obtained on cooling, consisting mainly of lithium disulphide, was dried at 70° in an evacuated short wide tube connected to the pump, a vessel containing phosphoric oxide intervening. The product was powdered, sulphur was removed by extraction with carbon disulphide, and the residue thoroughly washed with ether and dried [Found: Li = 10·83; S (total) = 49·14; S (polysulphide) = 24·56. $Li_2S_2,C_2H_5{\cdot}OH$ requires Li = 11·19; S (total) = 51·71; S (polysulphide) = 25·80%]. The substance contained about 4 per cent. of impurity, probably lithium ethoxide resulting from alcoholysis of the compound during the drying of the jelly. It was observed that the rate at which alcohol was removed materially affected the sulphur content of the final product. Unless the alcohol was driven off rapidly, the sulphur value finally obtained was always low.

The disulphide thus obtained was a greenish-yellow powder, easily and completely soluble in water and readily soluble in alcohol. In these respects it resembles the tetrasulphide rather than the

disulphide of sodium. The alcoholic solution slowly dissolves more sulphur, forming a deep red solution from which, however, no higher polysulphide could be isolated. Both alcoholic and aqueous solutions of the disulphide oxidise on standing and sulphur is deposited. Ether, carbon disulphide, and organic solvents generally are without action on the substance. Attempts to precipitate the anhydrous disulphide from alcoholic solutions by the addition of ether were not successful, a red oil being obtained which could not be made to crystallise and appeared to be an alcoholate (compare sodium tetrasulphide; Rule and Thomas, J., 1914, **105**, 177).

When heated in an open tube, the disulphide darkens and alcohol, hydrogen sulphide, and sulphur are expelled; thereafter, at about 400°, signs of melting can be observed.

Owing to alcoholysis taking place, the molecular complexity of the substance in boiling alcohol could not be determined.

*Behaviour with Allyl Iodide.*—The dried substance (2 gms.), dry ether (50 c.c.), and a slight excess of allyl iodide were shaken in dry hydrogen for 5 days; the residue contained no sulphur. The ethereal solution was extracted with water to remove lithium iodide, dried over calcium chloride, and distilled under reduced pressure. The first fraction consisted of ether and allyl iodide. A small amount of polysulphide came over at 84—86°/16 mm., but the greater portion of the polysulphide formed a double compound with allyl iodide which decomposed at a higher temperature. A mixture of allyl iodide and the polysulphide then came over, but the distillate consisted almost entirely of the latter substance, a colourless oil (yield *ca.* 70%) [Found: S = 42·77. $(C_3H_5)_2S_2$ requires S = 43·82%]. In view of the difficulty of removing the last traces of allyl iodide from the liquid, this result is considered to be satisfactory.

The oil had a characteristic garlic-like smell. It was insoluble in water, but readily soluble in alcohol. When it was treated with an alcoholic solution of mercuric chloride, no precipitate formed, but on dilution with water a heavy white powder was thrown down. This substance was a double compound of the polysulphide with mercuric chloride, and this reaction is characteristic of the disulphides.

## *Summary.*

1. Lithium monosulphide containing a trace of polysulphide has been prepared from lithium hydrosulphide alcoholate. Its properties closely resemble those of the corresponding sodium compound.

2. The solubility of sulphur in 0·5*N*-alcoholic solutions of lithium hydrosulphide has been measured at 80°, 25°, and 15°.

3. The only lithium polysulphide obtained is the disulphide, $Li_2S_2,C_2H_5{\cdot}OH$.

4. The constitution of lithium disulphide is shown to be similar to that of sodium disulphide, diallyl disulphide being formed on treatment with allyl iodide.

In conclusion, the authors wish to acknowledge their indebtedness to Professor E. C. C. Baly, C.B.E., F.R.S., for his interest and kindly criticism during the progress of this investigation, and also to Mr. R. W. Riding, B.Sc., for much help in connexion with the experimental portions of the work.

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## CCXCIII.—*Studies in the Organic Polysulphides. Part II. The Action of Anhydrous Potassium Pentasulphide on Allyl Iodide and on some Aromatic Halogen Compounds.*

By JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING.

THE reactions are described which occur between anhydrous potassium pentasulphide and the typical unsaturated compound allyl iodide on the one hand, and, on the other, benzyl chloride and *p*-bromonitrobenzene.

It is remarkable that diallyl pentasulphide does not appear to have been isolated from any natural source (compare Semmler, *Arch. Pharm.*, 1893, **230**, 434), for it is the easiest of the allyl polysulphides to obtain synthetically. It is also interesting because of the possibility it offers of the formation of crystalline derivatives by addition at the double bonds. A tetraiodide, $C_6H_{10}I_4S_5$, was, in fact, readily obtained as a very insoluble, black powder. This is additional evidence in favour of the view that the pentasulphides are definite compounds rather than stable solutions of sulphur in lower polysulphides.

The reaction between bromine and diallyl pentasulphide follows a somewhat different course. Instead of a tetrabromo-pentasulphide, an oil, which appears to be a tribromo-derivative, was obtained, the exact constitution of which has not yet been determined. This substance reacts readily with piperidine with the removal of bromine and the formation of a double compound of uncertain composition. This reaction led to the discovery of the double compounds of organic pentasulphides with piperidine, the only double compounds of saturated pentasulphides which have as yet been isolated. These, too, are uncrystallisable oils.

With regard to the aromatic sulphides, although straight-chain or single-branched-chain polysulphides have been prepared as high as the tetrasulphide by the action of halogen or oxyhalogen derivatives of sulphur on mercaptides or mercaptans (Bottger, *Annalen*, 1884, **223**, 348; Holmberg, *ibid.*, 1908, **359**, 81; Tasker and Jones, J., 1909, **95**, 1910; Smythe and Forster, J., 1910, **97**, 1195; Chakravarti, J., 1923, **123**, 964), in no case have aromatic pentasulphides been obtained. Moreover, in the study of the interaction of aromatic halides and inorganic polysulphides, no advance has been made since Blanksma (*Rec. trav. chim.*, 1901, **20**, 121) obtained a straight-chain tetrasulphide by the action of sodium tetrasulphide on *o*-bromonitrobenzene. However, *benzyl pentasulphide* has now been prepared by the method previously described (J., 1923, **123**, 3271); it is an oil even at — 80°, whereas Smythe and Forster's straight-chain tetrasulphide is a well-defined solid, m. p. 49°.

The interaction between *p*-bromonitrobenzene and potassium pentasulphide gave neither pentasulphide nor disulphide, but about a 20 per cent. yield of a complex of 4 : 4′-dinitrodiphenyl disulphide with 2 mols. of potassium ethoxide. It is hoped to continue this work in order to elucidate the exact position at which the potassium ethoxide is combined.

The method employed for the preparation of the compounds now mentioned was the same as that already described (*loc. cit.*, p. 3275). The reaction in the case of diallyl pentasulphide was over in about 5 days, dibenzyl pentasulphide required about 5 weeks, whilst in an experiment in which naphthyl bromide was used no noticeable change had taken place at the end of 3 months. The purification of the products obtained offered no serious difficulty, and the methods employed are described in the experimental part.

No attempt has been made to discuss the structure of the polysulphides in the light of the observations which have been made. It has been thought better first to present the facts. Questions of structure will be made the subject of a separate communication.

## Experimental.

*Diallyl Pentasulphide.*—The crude product (S = 51·85 per cent.) prepared by the interaction of allyl iodide and anhydrous potassium pentasulphide by the method used in the case of the corresponding propyl derivatives (Riding and Thomas, *loc. cit.*), was heated in a vacuum at 80° for about 24 hours, whereby allyl disulphide, solvent, and unchanged halide were removed and the pentasulphide was obtained (Found : S = 66·2. Calc., S = 66·1 per cent.).

A better product can be prepared by keeping the crude polysulphide in an exhausted desiccator for about 6 weeks, when the

volatile products are removed without fear of any possible decomposition of the pentasulphide (Found : S = 65·92; C = 29·97; H = 4·09. Calc., S = 66·1; C = 29·75; H = 4·14 per cent.). Yield 91 per cent.

*Diallyl pentasulphide* is a light yellow, highly refractive oil, $d^{18°}$ 1·249, with a very characteristic garlic odour. It is miscible with ether, chloroform, hexane, carbon disulphide, or benzene, slightly soluble in alcohol or acetone, but practically insoluble in water, although volatile in steam without excessive decomposition taking place. It does not form additive compounds with silver nitrate or mercuric iodide, but it slowly reacts with mercuric chloride to give very insoluble products.

*Diallyl Pentasulphide Tetraiodide.*—The black precipitate formed from iodine and the pentasulphide in chloroform is insoluble in all common solvents, including nitrobenzene and aniline. After treatment with caustic soda and potassium iodide and extraction with boiling chloroform, the *tetraiodide* is obtained as a black, lustrous, brittle powder, m. p. about 92° (Found : I = 67·88; S = 22·1. $C_6H_{10}I_4S_5$ requires I = 67·73; S = 21·5 per cent.). A preliminary extraction with carbon disulphide showed the absence of free sulphur, thus directly proving the identity of these pentasulphides. Attempts to prepare double iodides were unsuccessful.

*The Action of Bromine on Diallyl Pentasulphide.*—After interaction between bromine (slight excess) and the pentasulphide in chloroform, a large excess of light petroleum was added to the cooled product, partial solution taking place. The soluble portion was diallyl disulphide tetrabromide (Blanksma, *loc. cit.*) (Found : Br = 67·8; S = 14·76. Calc., Br = 68·6; S = 13·7 per cent.). The insoluble portion, a viscous liquid, was dissolved in chloroform, treated with dry ammonia, and partly precipitated with pentane. The portion remaining in solution was not a tetrabromide; the authors believe it to be a tribromide, $C_6H_9Br_3S_5$ (Found : Br = 50·5; S = 32·22. $C_6H_{10}Br_4S_5$ requires Br = 56·9; S = 28·45. $C_6H_9Br_3S_5$ requires Br = 49·8; S = 33·2 per cent.). The substance reacted with piperidine in benzene, piperidine hydrobromide being precipitated. The filtrate was concentrated and treated with light petroleum in large excess. From the viscous, dark brown oil obtained, chloroform extracted an oil, probably bromopiperidine (Found : Br = 48·5. Calc., Br = 48·7 per cent.). The black, insoluble, amorphous residue, m. p. 192—195°, still contained bromine and sulphur in the ratio 3 : 5 and was possibly a double compound of diallyl pentasulphide dibromide and dibromopiperidine (Found : Br = 45·23; S = 30·40; C = 19·40; H = 3·55. $2C_6H_8Br_2S_5,C_5H_9NBr_2$ requires Br = 46·01; S = 30·68; C = 19·56; H = 2·4 per cent.).

*Diallyl Pentasulphide Tripiperidine.*—The viscous red oil immediately obtained from the pentasulphide and piperidine in ether was heated in a vacuum at 70° for 24 hours (Found: S = 31·89; $C_5H_{11}N$ = 51·12. $C_6H_{10}S_5,3C_5H_{11}N$ requires S = 31·19; $C_5H_{11}N$ = 51·31 per cent.). The polysulphide was regenerated on addition of water or hydrogen chloride.

*Dibenzyl Pentasulphide.*—Potassium pentasulphide (5 gms.) and benzyl chloride (5·3 gms.) were shaken in dry ether, air and moisture being excluded. After 6 weeks, the ether was distilled, benzyl chloride removed by heating at 80° in a vacuum for 24 hours, and the polysulphide oil (S = 42 per cent.) extracted several times with absolute alcohol to remove any disulphide, and then freed from alcohol by vacuum drying (Found: C = 49·06; H = 4·03; S = 46·34. $C_{14}H_{14}S_5$ requires C = 49·12; H = 4·13; S = 46·75 per cent.).

*Dibenzyl pentasulphide*, a pale yellow, heavy oil practically insoluble in absolute alcohol, is by far the most stable pentasulphide so far obtained; it is decomposed very slowly by boiling water, and is not volatile in steam.

With piperidine, dibenzyl pentasulphide forms a red oily *tripiperidine* compound, similar in properties to the corresponding allyl and propyl derivatives (Found: S = 26·7. $C_{14}H_{14}S_5,3C_5H_{11}N$ requires S = 26·8 per cent.). This compound undergoes atmospheric oxidation after a few days, benzoylpiperidine being formed.

The formation of these additive compounds, which are not produced in the case of the disulphides, points to union between the piperidine molecules and three atoms of sulphur which are differently combined from the remaining two atoms in the pentasulphide.

*Action of Potassium Pentasulphide on* p-*Bromonitrobenzene. 4 : 4′-Dinitrodiphenyl Disulphide.*—From 0·5 gm. of anhydrous potassium pentasulphide and 8·5 gms. of *p*-bromonitrobenzene, reacting for one month, potassium bromide and a red, flocculent precipitate were produced. The ether was distilled off; the ether-soluble residue contained only *p*-bromonitrobenzene. The final residue was extracted with carbon disulphide and then with hot alcohol, which dissolved the red compound. The solution was concentrated, cooled (in the first experiment only, a few white, cubic crystals separated, m. p. 136—138°, after recrystallisation from alcohol), and dry benzene (20 vols.) added. The yellow, crystalline precipitate thus obtained was purified by dissolution and reprecipitation. It contained no bromine. Two preparations gave on analysis K = 17·04, 16·69; S = 16·69, 13·6 or K : S :: 1 : 1. It was first thought that these divergent results might possibly be due to solvent, but this idea had to be abandoned, since, after drying

at 80° in a vacuum for several hours, the substance retained its potassium value unchanged (16·83 %). On addition of water, the substance dissolved easily, giving a deep yellow solution which turned colourless with acid and yellow again with alkali, and from which a potassium-free compound (m. p. 76°) separated out if the solution was sufficiently concentrated. This was, however, more easily prepared by passing dry hydrogen chloride into an ethereal suspension of the potassium complex, when potassium chloride was removed and the potassium-free compound obtained by crystallisation in long, silky needles, m. p. 74°.

Attempts to obtain carbon and hydrogen values were very unsatisfactory, since the compound decomposed on heating strongly and appeared to be decomposing even at the ordinary temperature. Thus, after the substance had been kept for a week in a vacuum over phosphoric oxide, the melting point rose to 178—180°, that required for 4 : 4′-dinitrodiphenyl disulphide (Wohlfahrt, *J. pr. Chem.*, 1902, [ii], **66**, 551) (Found : C = 45·8; H = 3·55; S = 19·7. Calc., C = 46·2; H = 2·59; S = 20·5 per cent.).

On reviewing the work some time later, the possibility of potassium ethoxide compounds was noticed, although it was difficult to understand their formation without a trace of alcohol being present. 4 : 4′-Dinitrodiphenyl disulphide was therefore warmed with alcoholic sodium ethoxide, the quantity of which was slightly less than that required to form the compound $(NO_2{\cdot}C_6H_4)_2S_2,2EtONa$. The disulphide dissolved, and on the addition of benzene the sodium complex was precipitated as a beautifully yellow, feathery mass. This behaved in every way analogously to the corresponding potassium complex, and further to prove the similarity between these two compounds the sodium-free complex was prepared and found to melt at 73—74° (Found : S = 14·42; Na = 10·4. Required : S = 15·09; Na = 10·36 per cent.).

*Summary.*

1. The action of anhydrous potassium pentasulphide on allyl iodide and on certain aromatic halogen derivatives has been investigated. Diallyl and dibenzyl pentasulphides have in this way been prepared in about 90 per cent. yield.

2. These compounds closely resemble the alkyl pentasulphides in their properties, but they are more stable. Like them, they form with piperidine additive compounds of the general formula $R_2S_5,3C_5H_{11}N$.

3. Diallyl pentasulphide also forms compounds with iodine and bromine having the formulæ $C_6H_{10}I_4S_5$ and $C_6H_9Br_3S_5$.

4. The action of potassium pentasulphide on *p*-bromonitro-

benzene, followed by purification with alcohol, results in the formation of a potassium salt, $(C_6H_4{\cdot}NO_2)_2S_2,2C_2H_5OK$. From this substance a disulphide containing alcohol, m. p. 74°, is obtained by the action of hydrochloric acid on a concentrated aqueous solution of the salt. The alcohol is rapidly given off and a disulphide, m. p. 178—180°, obtained.

In conclusion the authors desire to express their thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for providing the facilities for this investigation, and for his kindly interest and criticism during its progress, and to Mr. J. H. Jones, who has rendered valuable assistance in the experimental work.

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## CCXCIV.—*Cryoscopic Measurements with Nitrobenzene. Part II. The Variation of the Molecular Depression with Water Content.*

By FREDERICK STANLEY BROWN and CHARLES R. BURY.

BECKMANN and LOCKEMANN (*Z. physikal. Chem.*, 1907, **60**, 385) claim that the molecular depression of the freezing point of nitrobenzene depends on its water content: the normal value of this constant is 69, but with carefully dried nitrobenzene they got values up to 84. Böeseken and van der Eerden (*Rec. trav. chim.*, 1914, **33**, 301) were unable to obtain abnormally high values with dry nitrobenzene, but with the moist solvent they got a low value (58).

We are engaged in studying the influence of water on the association of solutes in nitrobenzene solution by the freezing-point method, and a knowledge of the variation of the molecular depression with the water content of the solvent is a necessary preliminary. The subject is also of interest owing to the discovery by Baker of the profound modification of the properties of liquids by traces of water.

As the result of work published in the first paper of this series (Roberts and Bury, J., 1923, **123**, 2037), we are able to approach the problem in a more quantitative manner than was possible to earlier investigators. In this paper was described a method of maintaining the water content of the solvent constant, by keeping it in contact with a salt hydrate pair or other substance of definite aqueous vapour pressure. Thus the water content can be kept

constant during any one series of determinations, and this constant water content can be varied at will from saturation to practically complete dryness by the choice of a suitable substance.

We have continued our observations to higher concentrations than are usually employed, with the object of forming an estimate of the errors involved in the determination of molecular weights in not very dilute solutions.

TABLE I.

Solute benzil (Molecular weight 210·1).

| Solute (gms.). | $\Delta t_u$. | $K$. | $k$. | Molecular weight from (1). | Molecular weight from (2) or (4). |
|---|---|---|---|---|---|
| *Series* 1. 18·22 Gms. of nitrobenzene, in presence of $P_2O_5$. | | | | | |
| 0·1238 | 0·222° | 68·6 | 56·0 | 210·2 | 209·3 |
| 0·3421 | 0·605 | 67·7 | 55·6 | 213·1 | 210·7 |
| 0·9188 | 1·604 | 66·8 | 55·9 | 216·0 | 209·7 |
| 1·7351 | 2·955 | 65·2 | 55·9 | 221·4 | 209·6 |
| 2·3496 | 3·924 | 63·8 | 55·9 | 225·8 | 209·9 |
| *Series* 2. 19·82 Gms. of nitrobenzene, in presence of $P_2O_5$. | | | | | |
| 0·2466 | 0·404° | 68·2 | 55·5 | 211·5 | 210·0 |
| 0·7676 | 1·238 | 67·1 | 55·8 | 214·9 | 210·1 |
| 1·5901 | 2·505 | 65·6 | 55·8 | 220·1 | 210·1 |
| 2·2791 | 3·523 | 64·3 | 55·8 | 224·3 | 210·0 |
| *Series* 3. 19·58 Gms. of nitrobenzene, in presence of $Na_2SO_4,0—10H_2O$. | | | | | |
| 0·5910 | 0·955° | 66·5 | 55·6 | 217·2 | 211·1 |
| 1·1310 | 1·811 | 65·9 | 55·9 | 219·2 | 209·5 |
| 1·2363 | 1·968 | 65·5 | 55·8 | 220·5 | 210·2 |
| 1·4605 | 2·313 | 65·2 | 55·9 | 221·6 | 209·8 |
| 1·6302 | 2·573 | 64·9 | 55·9 | 222·3 | 209·6 |
| 1·9512 | 3·054 | 64·4 | 56·0 | 224·2 | 209·3 |
| 2·2632 | 3·505 | 63·7 | 55·9 | 226·6 | 209·8 |
| *Series* 4. 19·57 Gms. of nitrobenzene, in presence of $Na_2SO_4,0—10H_2O$. | | | | | |
| 0·1442 | 0·237° | 67·6 | 55·8 | 213·7 | 210·2 |
| 0·3877 | 0·633 | 67·1 | 55·8 | 215·1 | 209·9 |
| 0·5992 | 0·975 | 66·9 | 56·0 | 215·8 | 209·2 |
| 1·7783 | 2·797 | 64·7 | 55·9 | 223·2 | 209·4 |
| 2·3790 | 3·682 | 63·6 | 55·9 | 227·0 | 209·3 |
| *Series* 5. 19·55 Gms. of nitrobenzene, in presence of water. | | | | | |
| 0·1728 | 0·285° | 67·7 | 56·0 | 213·1 | 208·0 |
| 0·5799 | 0·940 | 66·5 | 55·9 | 216·9 | 209·2 |
| 1·2142 | 1·929 | 65·2 | 55·9 | 221·2 | 209·4 |
| 1·9001 | 2·957 | 63·9 | 55·9 | 225·9 | 209·8 |
| 2·6314 | 4·016 | 62·6 | 55·9 | 230·3 | 209·6 |
| *Series* 6. 19·10 Gms. of nitrobenzene, in presence of water. | | | | | |
| 0·4304 | 0·716° | 66·7 | 55·3 | 216·3 | 209·3 |
| 0·9683 | 1·585 | 65·7 | 55·9 | 219·8 | 209·5 |
| 1·5766 | 2·535 | 64·5 | 55·9 | 223·8 | 209·5 |
| 1·9893 | 3·153 | 63·6 | 55·8 | 227·0 | 210·0 |

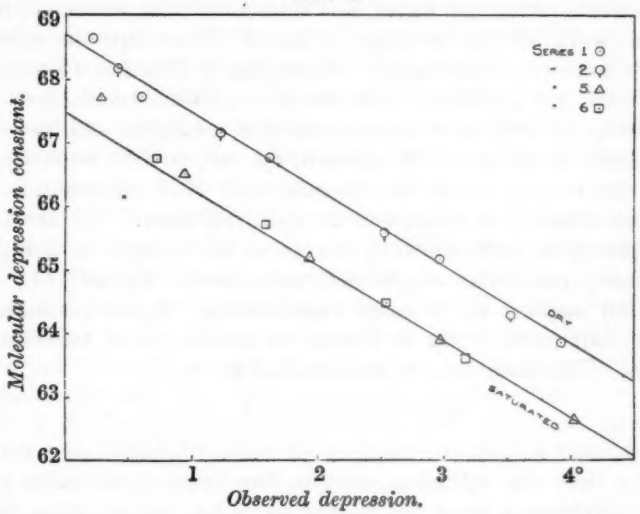
The results given in Table I, with benzil as solute, are typical. The first two series are duplicate determinations in the dry solvent,

in the presence of phosphorus pentoxide; the third and fourth in partly saturated nitrobenzene, in the presence of $Na_2SO_4,0—10H_2O$; the last two are in nitrobenzene, in contact and fully saturated with water. The values of the molecular depression constant ($K$), shown in the third column, have been calculated from the usual Raoult-van't Hoff formula :—

$$\Delta t_u = 100\, W_u K / W_v M_u \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\Delta t_u$ is the observed depression due to the addition of the solute, $W_u$ the weight, and $M_u$ the molecular weight of the solute, and $W_v$ the weight of the dry solvent. Assuming a possible error

FIG. 1.




of 0·003° in the experimental determination of the depression, the calculated values of $K$ are uncertain to an extent of 1% when the depression is 0·3°, and 0·1% when it is 3·0°.

In the figure the values of $K$ are plotted against the depressions. The results in partially saturated nitrobenzene are omitted for the sake of clearness : they lie between and parallel to those obtained with the dry, and those with the saturated solvent. The figure clearly shows that the molecular depression does depend on the water content, but the variation—1·2 units—is much less than was found by Beckmann and Lockemann. Benzil was one of the solutes used by them in their work on this point : the other, iodine, we have found to be abnormal (it appears to be associated) in nitrobenzene, as in so many other solvents, and we hope to discuss it more fully in a further communication. Since we have quanti-

tatively confirmed with two other solutes the variation of $K$ found with benzil, and since we have a satisfactory theoretical explanation of this variation, we can only attribute the much greater variations found by the earlier workers to change of water content of the solvent during the course of an experiment, between the determination of the freezing point of the solvent and that of the solution.

The figure also shows how unsatisfactory the Raoult-van't Hoff equation is: $K$ is not constant, and only has its theoretical value at infinite dilution in the pure dry solvent. For many years the advantages of using equations based on the "ideal" rather than the "gas-pressure" theory of solutions have been urged in theoretical papers, and an equation of this type, involving the specific heats of ice and water, has been used with success in recent accurate work on the freezing points of dilute aqueous solutions (see, for example, Washburn, "Principles of Physical Chemistry," 1915, chap. xiv.). Where sufficiently accurate specific heat data are lacking, as with most organic solvents, a simpler and less accurate formula is available (Washburn, *op. cit.*, p. 172, equation 48), which differs only from the Raoult-van't Hoff equation in that the concentration is expressed in mol. fractions. We are aware of no practical work showing the great advantages of using this in ordinary molecular-weight determinations: Fawsitt (J., 1919, **115**, 790) applied it to some experimental figures obtained by Fischer, but gave it up in favour of an empirical two-constant formula. The equation we recommend is:—

$$\Delta t_u = kn_u/(n_u + n_v) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $n_u$ and $n_v$ are the number of mols. of solute and solvent. In order that this equation shall be the same as equation (1) at infinite dilution, $k$ must be related to $K$ by the equation $M_v k = 100K$, where $M_v$ is the molecular weight of the solvent. Thus, taking 68·7 as the most probable value of $K$ for nitrobenzene, $k$ becomes 55·8.

Formula (2) is only applicable to the dry solvent; it requires modification before applying to moist solvents. In this case there are two solutes, benzil and water ($n_w$ mols.). The depression now becomes the sum of two depressions, $\Delta t_u$, the observed depression due to the benzil, *i.e.*, the difference between the freezing points of the moist solvent and of the moist solution, and $\Delta t_w$, the depression due to water, *i.e.*, the difference between the freezing points of the dry and of the moist solvent. This latter was determined in the first paper for different degrees of moisture obtained by use of several salt hydrate pairs. Thus equation (2) becomes

$$\Delta t = \Delta t_u + \Delta t_w = k(n_u + n_w)/(n_u + n_v + n_w) \quad . \quad . \quad (3)$$

When $n_u = 0$, $\Delta t_u = 0$, and equation (3) becomes

$$\Delta t_w = kn_w/(n_v + n_w).$$

On substituting the appropriate numerical values of $\Delta t_w$ and $k$ and simplifying, one can write $n_w = Cn_v$, the factor $C$ having the value 0·00924 when the solvent is fully saturated with water, and 0·00582 when it is partially saturated in the presence of $Na_2SO_4,0—10H_2O$. Thus $n_w$ can be eliminated from equation (3) :—

$$\Delta t = \Delta t_u + \Delta t_w = k[n_u + Cn_v]/[n_u + (1 + C)n_v] \quad . \quad . \quad (4)$$

For the dry solvent, $C$ and $\Delta t_w$ are 0, and this equation becomes identical with (2).

By the use of salt hydrate pairs or free water, and by elimination of the concentration of water in this way, the difficulty of measuring the concentration of the water, and possible errors due to its association are avoided. We are really keeping the active mass of the water, rather than its concentration, constant; the latter may vary with addition of solute,* but since the depression depends on the active mass, the difficulty is avoided.

Values of $k$ calculated from equations (2) and (4) are shown in the fourth column in Table I; in the fifth column are the molecular weights calculated from equation (1), assuming $K$ to be 68·7, and in the sixth are those from equations (2) or (4), assuming a value of 55·8 for $k$. The experimental error is somewhat magnified in the arithmetical process of calculating molecular weights from equations (2) and (4). The constancy of the molecular weight and of $k$ derived from these equations, and their close agreement with theory, are in favourable contrast with the corresponding values from the Raoult-van't Hoff equation.

It is obvious that the van't Hoff factor $K$ must change with the water content of the solvent, because the van't Hoff equation itself is untrue. According to equation (2), which has been found approximately true, the depression caused by addition of a quantity of solute to a quantity of solvent depends, not only on these quantities, as in the van't Hoff equation, but also on the amount of solute already present. This is true when the solvent is moist, and the solute already present is water. Consequently, the depression and the factor $K$ must be functions of the water content of the solvent.

* In the first paper, the change in the solubility of water with the addition of solute was discussed, and it was pointed out that it could be calculated from Nernst's law of the lowering of solubility. This is, of course, wrong; the law applies to the lowering of the solubility of nitrobenzene in water, not vice versa. The solubility should be slightly increased, in the same way as the vapour pressure of a liquid is increased by addition of a neutral gas to the system (Callendar, *Z. physikal. Chem.*, 1908, **63**, 645).

Assuming equations (2) and (4) to be true, we have calculated how $K$ should vary with the depression in the dry, and in the saturated solvent. The results are indicated by the lines in the figure : they agree with the observed values within the limits of experimental error.

## Table II.

### Solute naphthalene (Molecular weight 128·1).

*Series* 1. 22·60 Gms. of nitrobenzene, in presence of $P_2O_5$.

| Solute (gms.). | $\Delta t_m$. | $K$. | $k$. | Molecular weight from (1). | Molecular weight from (2) or (4). |
|---|---|---|---|---|---|
| 0·1777 | 0·418° | 68·1 | 55·7 | 129·3 | 128·3 |
| 0·4238 | 0·987 | 67·4 | 55·7 | 130·5 | 128·2 |
| 0·7795 | 1·793 | 66·6 | 55·9 | 132·2 | 127·9 |
| 1·2035 | 2·713 | 65·2 | 55·7 | 134·9 | 128·3 |
| 1·6342 | 3·627 | 64·2 | 55·8 | 137·1 | 128·0 |

*Series* 3. 20·03 Gms. of nitrobenzene, in presence of $Na_2SO_4,0—10H_2O$.

| | | | | | |
|---|---|---|---|---|---|
| 0·0820 | 0·221° | 69·1 | 56·3 | 127·3 | 125·5 |
| 0·3608 | 0·939 | 66·7 | 55·8 | 131·8 | 128·1 |
| 0·5584 | 1·441 | 66·2 | 55·9 | 132·9 | 128·0 |
| 0·7282 | 1·858 | 65·4 | 55·7 | 134·4 | 128·4 |
| 0·9517 | 2·409 | 64·9 | 55·8 | 135·5 | 128·1 |
| 1·1562 | 2·914 | 64·6 | 56·1 | 136·0 | 127·5 |

*Series* 5. 19·81 Gms. of nitrobenzene, in presence of water.

| | | | | | |
|---|---|---|---|---|---|
| 0·1095 | 0·294° | 68·1 | 55·9 | 129·1 | 126·1 |
| 0·2847 | 0·749 | 66·7 | 55·8 | 131·8 | 127·6 |
| 0·6398 | 1·650 | 65·4 | 55·8 | 134·5 | 128·0 |
| 1·0303 | 2·611 | 64·3 | 55·8 | 136·8 | 127·9 |
| 1·4817 | 3·696 | 63·3 | 56·0 | 139·0 | 127·4 |

## Table III.

### Solute α-nitronaphthalene (Molecular weight 173·1).

*Series* 1. 21·13 Gms. of nitrobenzene, in presence of $P_2O_5$.

| Solute (gms.). | $\Delta t_m$. | $K$. | $k$. | Molecular weight from (1). | Molecular weight from (2) or (4). |
|---|---|---|---|---|---|
| 0·2307 | 0·431° | 68·3 | 55·9 | 174·0 | 172·6 |
| 0·6902 | 1·268 | 67·2 | 55·9 | 177·0 | 172·9 |
| 1·2811 | 2·310 | 65·9 | 55·9 | 180·3 | 172·8 |
| 1·8022 | 3·192 | 64·8 | 55·8 | 183·5 | 173·1 |

*Series* 3. 19·56 Gms. of nitrobenzene, in presence of $Na_2SO_4,0—10H_2O$.

| | | | | | |
|---|---|---|---|---|---|
| 0·1554 | 0·309° | 67·3 | 55·7 | 176·6 | 173·6 |
| 0·3803 | 0·753 | 66·7 | 55·8 | 178·2 | 172·9 |
| 0·8603 | 1·676 | 65·9 | 55·9 | 180·3 | 172·8 |
| 1·3095 | 2·506 | 64·8 | 55·8 | 183·5 | 173·2 |
| 1·7135 | 3·245 | 64·1 | 56·0 | 185·6 | 172·6 |

*Series* 5. 19·58 Gms. of nitrobenzene, in presence of water.

| | | | | | |
|---|---|---|---|---|---|
| 0·1784 | 0·353° | 67·1 | 55·8 | 177·4 | 172·9 |
| 0·4506 | 0·883 | 66·4 | 55·9 | 179·1 | 173·2 |
| 0·7021 | 1·362 | 65·7 | 55·8 | 180·9 | 173·2 |
| 1·1365 | 2·177 | 64·9 | 55·9 | 183·2 | 172·8 |
| 1·4007 | 2·658 | 64·3 | 55·9 | 184·9 | 172·8 |
| 1·6278 | 3·072 | 63·9 | 56·0 | 186·0 | 172·4 |
| 1·8595 | 3·477 | 63·3 | 56·0 | 187·7 | 172·6 |

TABLE IV.

Solute anisole (Molecular weight 108·1).

*Series* 1. 20·00 Gms. of nitrobenzene, in presence of $Na_2SO_4,0—10H_2O$.

| Solute (gms.). | $\Delta t_m$. | $K$. | $k$. | Molecular weight from (1). | Molecular weight from (2) or (4). |
|---|---|---|---|---|---|
| 0·0966 | 0·300° | 67·2 | 55·6 | 110·6 | 108·8 |
| 0·1991 | 0·620 | 67·3 | 55·9 | 110·4 | 107·8 |
| 0·3413 | 1·053 | 66·7 | 55·9 | 111·3 | 107·9 |
| 0·4895 | 1·497 | 66·1 | 55·9 | 112·3 | 108·0 |
| 0·8132 | 2·447 | 65·0 | 55·9 | 114·1 | 107·8 |
| 1·1878 | 3·507 | 63·8 | 56·0 | 116·3 | 107·7 |

TABLE V.

Solute *s*-tetrachloroethane (Molecular weight 168·0).

*Series* 1. 20·32 Gms. of ntirobenzene, in presence of $Na_2SO_4,0—10H_2O$.

| Solute (gms.). | $\Delta t_m$. | $K$. | $k$. | Molecular weight from (1). | Molecular weight from (2) or (4). |
|---|---|---|---|---|---|
| 0·2394 | 0·473° | 67·4 | 55·9 | 171·2 | 167·8 |
| 0·3519 | 0·689 | 66·8 | 55·7 | 172·8 | 168·6 |
| 0·5057 | 0·989 | 66·5 | 55·9 | 173·0 | 168·5 |
| 0·6588 | 1·279 | 66·2 | 55·8 | 174·2 | 168·3 |
| 0·8073 | 1·561 | 66·0 | 55·8 | 175·0 | 168·1 |
| 1·0584 | 2·040 | 65·8 | 56·1 | 175·5 | 167·3 |

In Tables II and III are given similar results with naphthalene and α-nitronaphthalene as solutes, in dry, partially saturated, and saturated nitrobenzene: in Tables IV and V are the results obtained with anisole and *s*-tetrachloroethane in partly saturated nitrobenzene only. These solutes were chosen as representatives of the most diverse types: as with benzil, each series was confirmed by a duplicate series, but these are omitted for lack of space. The results quoted confirm the conclusions reached with benzil.

## EXPERIMENTAL.

The usual Beckmann method was employed, and the use of salt hydrate pairs to keep the water content constant has been described in the previous paper. In working with the dry solvent, a current of dry air was passed through the apparatus as an additional precaution.

Accurate and consistent results can only be obtained with considerable practical experience of the method and careful attention to details. The bath temperature should be less than 2·0° below the freezing point of the solution; a supercooling of more than half a degree must be avoided, the inoculation method being used if necessary. Sunlight must not be allowed to fall directly on to the apparatus.

In using the salt hydrate method, the partly frozen solution must not be warmed by the hand preparatory to redetermining

the freezing point, but must be allowed to warm in the air slowly and with constant stirring, until its temperature is not more than a degree above the freezing point. The first determination of the freezing point of a solution is invariably low, the second often a little low, but if the solution is not allowed to warm between determinations, a constant value is then reached. Thus, successive determinations of the freezing point of a solution gave these results: 3·052°, 3·065°, 3·070°, 3·072°, 3·072°. The probable reason for this is that at first the solvent is saturated with water at room temperature; when cooled to the freezing point it is supersaturated, and only attains equilibrium slowly. It is quicker to freeze a solution directly in the outer bath and allow it to warm again until just above its freezing point before making the first determination.

All results quoted are based on at least two closely agreeing determinations of the freezing point, and we believe most of the depressions given to be accurate to 0·003°. It should be noted that all experimental errors tend to make the freezing point too low, and that it becomes increasingly difficult to get consistent results with depressions greater than 3·0°.

The purification of the nitrobenzene has been described in the first paper. All solutes and salt hydrates have been carefully purified by recrystallisation or distillation.

*Summary.*

The depression by several normal solutes of the freezing point of nitrobenzene of varying degrees of dryness has been studied up to concentrations of 0·06 mol. per 100 gms. of nitrobenzene.

The change of the molecular depression constant with water content of the solvent has been confirmed, but the authors differ considerably from previous workers in their estimate of the magnitude of this change.

An equation in which concentrations are expressed as mol. fractions has been found to represent the experimental results with much greater accuracy than the Raoult-van't Hoff equation, and to give a quantitative explanation of the change in the molecular depression constant.

We wish to express our thanks to the Department of Scientific and Industrial Research for a grant made to one of us (F. S. B.) which has enabled this work to be carried out.

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# CCXCV.—*The Ionisation Constant of Hypochlorous Acid.*

By FREDERICK GEORGE SOPER.

NOYES and WILSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1630), by measuring the conductivities of sodium hydroxide and sodium hypochlorite in aqueous solution, found a value, $6{\cdot}70 \times 10^{-10}$, for the acidic ionisation constant of hypochlorous acid fifty times as small as that obtained by Sand (*Z. physikal. Chem.*, 1904, **46**, 610) from measurements of the solubility of carbon dioxide in solutions of sodium hypochlorite.

In view of this large discrepancy, a determination has been made by an independent method which consists in an estimation of the free hypochlorous acid in a solution of sodium hypochlorite by partition of the hypochlorous acid between the aqueous solution and an aqueous vapour phase. The method is similar to that used by Naumann and Müller (*J. pr. Chem.*, 1906, [ii], **74**, 218) for the determination of the hydrolysis of sodium phenoxide and of ammonium salts (Naumann and Rücker, *ibid.*, p. 249).

The partition of hypochlorous acid between its aqueous solution and a contiguous aqueous vapour phase has been measured at 25°, by distillation of aqueous hypochlorous acid under diminished pressure and determination of the ratio of the concentration of acid in the distillate to that in the solution. The fact that this ratio was constant over the concentration range examined ($10^{-4}N$ to $4 \times 10^{-3}N$) is noteworthy, for it indicates that the molecular condition of hypochlorous acid in the gaseous state above a dilute hypochlorous acid solution is identical with that in the aqueous solution itself, which corresponds with the simple molecule HClO (Jakowkin, *Z. physikal. Chem.*, 1898, **29**, 613).

Noyes and Wilson state (*loc. cit.*) that on aspirating air through more concentrated solutions of hypochlorous acid chlorine monoxide and not hypochlorous acid is removed. This result might have been anticipated from the work of Goldschmidt (*Ber.*, 1919, **52**, [*B*], 753), who demonstrated the existence of the equilibrium $Cl_2O + H_2O \rightleftarrows 2HClO$ in aqueous solution and showed the constancy of the expression $[Cl_2O]/[HClO]^2$. In concentrated solutions of hypochlorous acid the concentration of chlorine monoxide becomes appreciable, and increases rapidly with increase in the hypochlorous acid concentration. If chlorine monoxide is more volatile than hypochlorous acid, the concentration of "active chlorine" may be largely determined by the distribution $[Cl_2O]_{gas}/[Cl_2O]_{soln.}$ = constant. For dilute solutions of hypochlorous acid (an $M/1000$-solution of the acid contains only $10^{-9}$ mol. of chlorine monoxide;

Goldschmidt, *loc. cit.*), the concentration of "active chlorine" in the gaseous phase will be mainly due to the partition of the hypochlorous acid molecules such that $[HClO]_{gas}/[HClO]_{soln.}$ = constant. At intermediate concentrations distribution according to both expressions is appreciable.

Examination of the results of Noyes and Wilson, however, reveals an error in the calculated thiosulphate titre of the chlorine monoxide carried forward by the air current. In experiment 2 of these authors, for example, the weight of gas collected was 0·1300 gm. = 0·001495 mol. if it were chlorine monoxide, requiring $1{\cdot}495 \times 4/0{\cdot}1513$ c.c. (since 1 mol. of $Cl_2O$ corresponds to 4 equivs. of iodine) = 39·5 c.c. of 0·1513*N*-thiosulphate. Actually 19·90 c.c. were required and the calculated value is given as 20·32 c.c. The discrepancy may possibly have been due to the absence of the necessary acid, in which case one-half of the hypochlorite would have formed iodate. (On addition of chlorine monoxide to fairly concentrated aqueous potassium iodide, the iodate may even come out of solution: personal observation.) It is difficult otherwise to obtain a meaning for the observed titres, which agree well with the values calculated by these authors. The experiments cannot be explained on the assumption that the air removed hypochlorous acid, for this substance is not sufficiently volatile to be carried forward in such quantity by the amount of air employed, even assuming complete saturation. Even if the normality of the thiosulphate has been wrongly expressed, the excessive volatility of the removed gas, if it were chlorine monoxide, still requires explanation. For, from Goldschmidt's results, the concentration of the monoxide in the solution is known and also, from Noyes and Wilson's work, the distribution of chlorine monoxide between air and its aqueous solution. It is easily shown from these results that the solubility in water of chlorine monoxide molecules, as such, is less than that of hydrogen, although its boiling point is more than 200° higher.

No attempt was made to measure the basic ionisation constant of hypochlorous acid. It is probably exceedingly small, being $4{\cdot}5 \times 10^{10}$ times less than the ionisation constant of chlorine into positive and negative chlorine ions (see Stieglitz, *J. Amer. Chem. Soc.*, 1901, **23**, 797). This follows easily from the known value of the hydrolysis constant of chlorine in aqueous solution (Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613).

## Experimental.

An aqueous solution of sodium hypochlorite was not prepared from the crystalline salt (Muspratt and Smith, *J. Soc. Chem. Ind.*,

1898, **17**, 1096; 1899, **18**, 210; Applebey, J., 1919, **115**, 1106) on account of the isomorphism of the hypochlorites and hydroxides (Orton and Jones, J., 1909, **95**, 751). A purer solution was obtained by mixing equivalent quantities of sodium hydroxide and hypochlorous acid, the latter having been prepared by leading chlorine monoxide into water, whereby the formation of hydrochloric acid was avoided. The chlorine monoxide was prepared from chlorine (from hydrochloric acid and permanganate) and yellow mercuric oxide. The solution of hypochlorous acid during preparation was carefully shielded from light to avoid any photochemical decomposition $HClO \longrightarrow HCl + O$ and contained a few grams of yellow mercuric oxide to remove any hydrochloric acid formed from unchanged chlorine. The mixture was kept at 1—2° over-night and then distilled rapidly into a blackened bottle, the distillate having the sweet ethereal smell associated with pure dilute hypochlorous acid, quite distinct from that of dilute chlorine monoxide. In more concentrated solutions the smell of chlorine monoxide predominates.

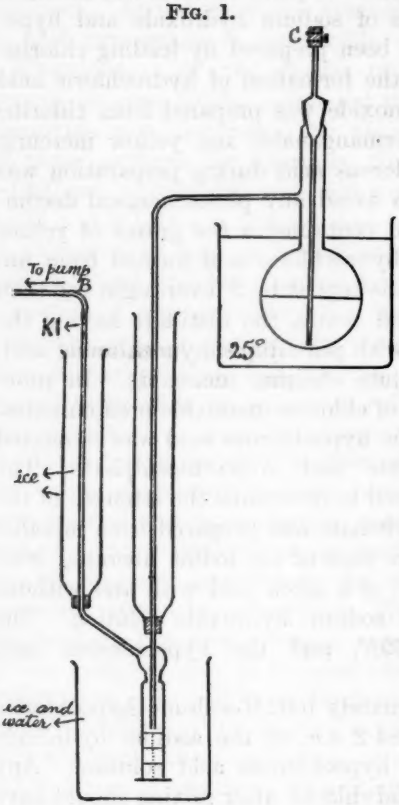
As soon as it was prepared, the hypochlorous acid was estimated with acidified potassium iodide and $N/50$-thiosulphate. The thiosulphate solution was also used to determine the strength of the sodium hydroxide (free from carbonate and prepared from metallic sodium), by the difference in the titre of the iodine liberated from iodide-iodate mixture by 20 c.c. of a stock acid with and without the addition of 10 c.c. of the sodium hydroxide solution. The sodium hydroxide was 0·07039$N$, and the hypochlorous acid 0·0618$M$.

A stock solution of approximately 0·02$M$-sodium hypochlorite was immediately made from 284·2 c.c. of the sodium hydroxide solution and 323·5 c.c. of the hypochlorous acid solution. Any slight conversion into chlorate and chloride after mixing should have had but a slight effect on the ratio of free hypochlorous acid to unhydrolysed sodium hypochlorite, for, in the formation of the chlorate, equivalent quantities of sodium- and hypochlorite-ions would have been removed.

*Method of Experiment.*—300 C.c. of the aqueous hypochlorite solution were distilled at 25° in the apparatus shown in the figure. Since the temperature controlled the vapour pressure, its constancy sufficiently defined the condition of the gaseous and of the aqueous phase, so long as the rate of ebullition was not too rapid. To ensure a uniform rate of distillation and to avoid any still-head effects other than those common to the entire series of experiments, the pressure in the neighbourhood of the pump was reduced to a constant 12 mm. The delivery tube, bent sharply at right angles, leading from the distilling flask to the graduated receiver was sur-

rounded by an ice jacket, as was also the tube, *B*, leading to the pump. A constriction in the tube *B* supported a few moist crystals of potassium iodide which served to detect any hypochlorous acid lost during the distillation. When 15 c.c. of the distillate collected, the distillation was stopped, the exact volume read off, and the thiosulphate titre found. The titre of the solution remaining in the flask was redetermined and the loss was found to correspond with the amount of hypochlorous acid in the distillate. In some cases this was relatively so small that there was no appreciable change in the titre of the solution. Experiments carried out on aqueous sodium hypochlorite in presence of an increasing excess of sodium hydroxide indicated that no unhydrolysed sodium hypochlorite was carried over into the receiver during the distillation.

FIG. 1.




The results of distilling hypochlorous acid solutions are given in Table I.

TABLE I.

| Conc. of acid. $M \times 10^3$. | C.c. of distillate. | Titre in c.c. of $N/500$-thio. | Conc. of HClO in distillate. $M \times 10^3$. | $\frac{[HClO]_{dist.}}{[HClO]_{soln.}}$ |
|---|---|---|---|---|
| 1·993 | 15·0 | 89·62 | 5·98 | 3·00 |
| 0·967 | 15·0 | 40·76 | 2·717 | 2·81 |
| 0·4661 | 14·9 | 18·76 | 1·258 | 2·70 |
| 0·3663 | 15·1 | 14·84 | 0·983 | 2·68 |
| 0·2605 | 15·0 | 10·40 | 0·693 | 2·66 |
| 0·1880 | 15·0 | 7·10 | 0·474 | 2·52 |
| 0·0561 | 15·2 | 2·39 | 0·157 | 2·80 |
| | | | Mean, omitting the value 3·00, | 2·69 |

The results of distillation of solutions of sodium hypochlorite at different concentrations, made from the stock solution by diluting with carbon dioxide-free water, are given in Table II: $K_h =$

[HClO] [NaOH]/[NaClO]. Two series of experiments were made with different stock solutions.

TABLE II.

| Conc. of hypochlorite. $M \times 10^3$. | C.c. of distillate. | Titre in c.c. of $N/500$-thio. | Deduced [HClO] in hypochlorite. $M \times 10^3$. | | $K_h \times 10^6$. |
|---|---|---|---|---|---|
| 1·101 | 14·98 | 1·26 | 0·0312 | | 0·912 |
| 0·4963 | 14·31 | 0·89 | 0·0231 | | 1·128 |
| 1·991 | 14·91 | 1·81 | 0·0451 | | 1·043 |
| 4·062 | 15·12 | 2·55 | 0·0627 | | 0·982 |
| 7·135 | 15·00 | 3·37 | 0·0835 | | 0·996 |
| 9·930 | 15·20 | 4·14 | 0·1012 | | 1·042 |
| | | | | Mean | 1·02 |
| 0·986 | 14·90 | 1·20 | 0·0299 | | 0·935 |
| 3·108 | 15·00 | 2·11 | 0·0523 | | 0·895 |
| 1·944 | 15·17 | 1·84 | 0·0451 | | 1·071 |
| 5·010 | 14·92 | 2·88 | 0·0717 | | 1·042 |
| 9·025 | 14·90 | 3·82 | 0·0953 | | 1·019 |
| | | | | Mean | 0·992 |

The mean value for the hydrolysis constant at 25° of the two series is $1·0 \times 10^{-6}$, corresponding with the value $1·0 \times 10^{-8}$ for the ionisation constant of hypochlorous acid.

*Summary.*

1. The ionisation constant of hypochlorous acid determined by estimation of the free hypochlorous acid in sodium hypochlorite solutions by a distillation method, is $1·0 \times 10^{-8}$.

2. The composition of the gaseous mixture obtained by aspirating air through hypochlorous acid solutions is discussed. It is shown that hypochlorous acid is itself slightly volatile. The results of Noyes and Wilson do not agree with their deductions.

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## CCXCVI.—*Some Electrochemical Aspects of the Oxidising Properties of Sulphur Dioxide.*

By SYDNEY RAYMOND CARTER and FRANK JAMES.

DETAILED study has recently been made of the reaction between sulphur dioxide and various metallic salts in acid solution. In the case of a mixture of ferrous and ferric chlorides, for example, two reactions may take place according to conditions (Wardlaw and Clews, J., 1920, **117**, 1093):

(I.) $2FeCl_3 + H_2SO_3 + H_2O = 2FeCl_2 + 2H_2SO_4 + 2HCl.$

(II.) $4FeCl_2 + H_2SO_3 + 4HCl = 4FeCl_3 + S + 3H_2O.$

An application of the methods of electrochemistry should enable us to generalise the conditions under which such reactions can take place, and moreover furnish an insight into the mechanism of reactions of the type II.

The problem may be studied from two points of view:

(*a*) Oxidation-reduction potentials, (*b*) reduction of sulphur dioxide at the cathode.

### (*a*) *Measurements of Electrical Potential.*

According to equations I and II, sulphur dioxide can undergo decomposition in two distinct ways and they may be summarised by the equations

(III.) $H_2SO_3 + 2OH' = H_2SO_4 + H_2O + 2\ominus$.

(IV.) $H_2SO_3 + 4H^{\cdot} = S + 3H_2O + 4\oplus$.

If these processes are reversible, the following types of electrodes (A and B) should exhibit definite potentials and give a measure of the free energy of the respective reactions III and IV.

(A.) (Pt) | $H_2SO_4$, $H_2SO_3$, $x$*N*-HCl.

(B.) (Pt) | $H_2SO_3$, S, $x$*N*-HCl.

Electrodes somewhat similar to type A have been studied by Bancroft (*Z. physikal. Chem.*, 1892, **10**, 387) and Neumann (*ibid.*, 1894, **14**, 228), but neither of these workers defined the conditions accurately. Later, Schaum (*Z. Elektrochem.*, 1901, **7**, 483, 523) and Schaum and Linde (*ibid.*, 1903, **9**, 406) dealt with this potential, the solution being neutral or slightly acid, and found that it was inaccessible under these conditions. A similar conclusion was reached by Lewis, Randall, and Bichowsky (*J. Amer. Chem. Soc.*, 1918, **40**, 360), who carried the sulphuric acid concentration up to 10*N*. Some measurements are recorded by Taitelbaum (*Z. Elektrochem.*, 1910, **16**, 286) on the potential of sulphur dioxide in concentrated sulphuric acid, but here the solvent is no longer water and the conditions are scarcely comparable with those of the present work. The evidence points to electrodes of type A being inaccessible, and this is not surprising since the electrode process represented by equation III is chemically irreversible (Volhard, *Annalen*, 1887, **242**, 93).

Electrodes of type B have not hitherto been studied exhaustively and appeared more likely to yield positive results, particularly in strongly acid solution, provided that sulphur is present in an active form. In this connexion it may be mentioned that Küster has observed (*Z. anorg. Chem.*, 1905, **44**, 430) that sulphur readily dissolves ionically in alkaline solution. The sulphur ions would,

however, be divalent sulphide anions S″, whereas in the case of electrode B we should require reversible solution with respect to cations which would probably be quadrivalent S⁽⁴⁺⁾.

*Experimental.*—The appropriate solutions were confined for some weeks in an atmosphere of nitrogen with electrodes of various kinds such as (*a*) smooth platinum foil, (*b*) platinised platinum, (*c*) glass coated with a thin film of platinum, (*d*) platinum foil coated with a thin film of electrolytically deposited sulphur. In some cases gentle agitation was maintained by means of an electromagnetic stirring device, which permitted positive sealing of the electrode vessel.

The free sulphur for electrodes of type (B) was either introduced as powdered rhombic sulphur or was precipitated in the electrode vessel by the addition of a small quantity of sodium sulphide.

The potentials measured were not constant enough to be taken as a basis for thermodynamic deduction, nevertheless they showed some measure of consistency and after a time attained to values which were roughly reproducible to within 0·05 volt.

The potentials appeared to be independent of the type of electrode employed and electrodes in the same vessel were in close agreement; moreover, although readily polarised, they slowly returned to their original value. Agitation of the electrolyte had no great influence.*

The presence of sulphur or the sulphate-ion of the sulphuric acid appeared to be without effect and unnecessary. On the other hand, it was clear that the total concentration of acid given by the hydrochloric acid was a factor which influenced the value of the potential.

The cell

$$(\mathrm{Pt}) \left| \begin{matrix} 0{\cdot}2N\text{-}H_2SO_3,\ 2N\text{-HCl} \\ 0{\cdot}2N\text{-}H_2SO_4,\ \text{Sulphur} \end{matrix} \right| N\text{-KCl} \left| \begin{matrix} \mathrm{HgCl} \\ N\text{-KCl} \end{matrix} \right| \mathrm{Hg}$$

showed an *E.M.F.* of + 0·08 volt, whilst a similar cell in which the 2*N*-HCl was replaced by 10*N*-HCl gave an *E.M.F.* of + 0·17 volt.

If we allow 0·560 volt for the normal calomel electrode, values of $e_a = + 0{\cdot}64$ and + 0·73 volt, respectively, are obtained for the sulphur dioxide half-cell, uncorrected for diffusion potential.

While there are no theoretical grounds for attaching a meaning to the above *E.M.F.* values, it is interesting to consider them in conjunction with other observations and compare them with the potentials for the ferrous-ferric chloride mixtures.

* Scobai (*Z. Elektrochem.*, 1903, **9**, 879) has studied certain oxidation potentials involving irreversible reactions and they appear to have exhibited characteristics similar to those here recorded.

TABLE I.

*Sulphur dioxide.*

| Nature of solution. | Potential in volt. |
|---|---|
| Neutral | 0·55 (I) |
| 2·0*N*-HCl | 0·64 (V) |
| 10·0*N*-HCl | 0·73 (V) |
| Conc. $H_2SO_4$ | 0·94 (II) |

TABLE II.

*Ferrous-ferric chlorides.*

| Nature of solution. | | Potential in volt. [$Fe^{III}$] =50%. | [$Fe^{III}$] =10%. | [$Fe^{III}$] =0·5%. |
|---|---|---|---|---|
| Neutral | 25° | 1·020 | 0·965 | 0·887 (III) |
| 0·1*N*-HCl | 17 | 0·987 | 0·932 | 0·854 (IV) |
| 2·0*N*-HCl | 17 | 0·923 | 0·868 | 0·790 (IV) |
| 4·0*N*-HCl | 17 | 0·877 | 0·823 | 0·744 (IV) |
| 10·0*N*-HCl | 17 | 0·740 | 0·685 | 0·605 (IV) |

(I) Schaum and Linde (*loc. cit.*). (II) Taitelbaum (*loc. cit.*). (III) Maitland, *Z. Elektrochem.*, 1906, **12**, 263. (IV) Carter and Clews, this vol., p. 1880. (V) Present authors.

Single electrode potentials in this paper are referred to the absolute scale.

The values in the table are not corrected for the potential differences at the KCl | acid junction. On the basis of the Henderson formula this correction would amount to about + 0·04 volt for hydrochloric acid solutions from 2*N* to 10*N*.

It will be noticed that an increase in acid concentration is accompanied by a rise in the sulphur dioxide potential and a diminution in the ferric-ferrous potential. In fact, between 2*N*- and 10*N*-acid there is a complete reversal of the oxidising and reducing relations of the two systems.

The curve of the sulphur dioxide potential, LM, has been plotted on the diagram of the ferrous-ferric potentials (Carter and Clews, *loc. cit.*, Fig. 1), and it will be seen that it follows the same form as the inert area ACE–B in which sulphur dioxide acts neither as a reducing nor as an oxidising agent.

The present sulphur dioxide potential curve is slightly displaced from the inert area, but this is not surprising, since the potentials were measured at room temperature whilst the inert area has been traced from data relating to the neighbourhood of 100°.

### (*b*) *Cathodic Reduction of Sulphur Dioxide.*

The decomposition of sulphur dioxide in acid solution by chemical reducing agents leads to the formation of sulphur, but since the electrode of type B does not readily exhibit a definite potential, it would appear that the primary reduction product is not sulphur, but a compound which ultimately yields sulphur as a final product of decomposition. A likely compound to suspect is hydrogen sulphide, since this gas is actually detected in some cases and a sulphide of the metal is produced when the conditions of the solubility product allow of it (see Table IV).

The interaction of hydrogen sulphide with sulphur dioxide would also account for the presence of sulphur, particularly in the upper parts of the flask.

The cathodic reduction of sulphur dioxide appeared to offer a convenient means of studying the reduction products, and the presence of hydrogen sulphide in the reduced solution might be tested by chemical reactions, for example, formation of lead, antimony, or mercuric sulphide.

FIG. 1.

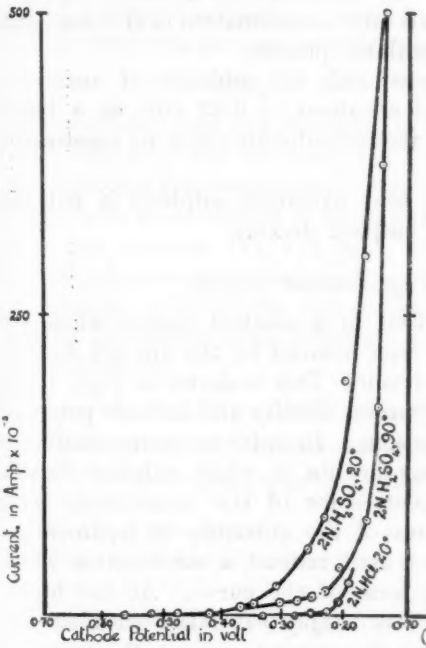
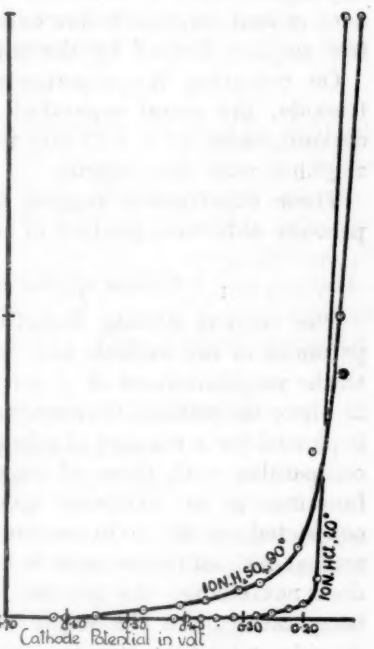



FIG. 2.




*Experimental.*—The electrolytic vessel used in the experiments consisted of a glass jar, 6 cm. in diameter, closed with a rubber stopper which carried two electrodes of platinum foil, 1 cm. square, an inlet and an outlet tube by which the air in the vessel could be replaced by nitrogen, and a syphon connexion tube for joining up with a standard half-element. The usual electrical circuits were employed. The chief solutions investigated were sulphur dioxide (or sodium sulphite) in hydrochloric or sulphuric acid (2*N* and 10*N*). On electrolysing at low current density in this apparatus, the first appearance of sulphur occurred when the potential of the cathode had been reduced to the neighbourhood of 0·37 volt, and it took the form of a faint veil near the cathode, but not in direct

contact with it. This cloud gradually extended towards the anode. Since sulphur in the colloidal condition carries a positive charge, this extension of the cloud towards the anode is the migration which might have been expected, under the influence of the current.

In order to test for the presence of hydrogen sulphide, lead chloride was added to the solution. The separation of sulphur was unaffected until the potential at the cathode had been reduced to a little below + 0·1 volt, when lead sulphide formed. Calculation shows that under these conditions metallic lead would be cathodically separated at + 0·07 volt. It seems, therefore, that the appearance of lead sulphide is due to a direct combination of free lead and free sulphur formed by the cathode process.

On repeating the experiment with the addition of antimony trioxide, the metal separated at about + 0·32 volt as a black deposit, whilst at + 0·27 volt the red sulphide made its appearance together with free sulphur.

These experiments suggest that hydrogen sulphide is not the primary reduction product of sulphur dioxide.

*Curves of Voltage–Current Density.*

The current density increased in a marked degree when the potential of the cathode had been reduced by the applied *E.M.F.* to the neighbourhood of + 0·1 volt. This is shown in Figs. 1 and 2, where the relation between current density and cathode potential is plotted for a number of solutions. In order to secure conditions comparable with those of experiments in which sulphur dioxide functions as an oxidising agent, some of the experiments were conducted at 90°. On account of the volatility of hydrochloric acid at 90°, sulphuric acid was used instead, a substitution which does not change the general form of the curve. At the higher temperature, the electrolyte was simply saturated with sulphur dioxide, whilst in the case of the experiments at the ordinary temperature it was found more convenient to dissolve pure sodium sulphite in the electrolyte.

*Mechanism of the Cathodic Reduction.*

It will be seen from the curves that the cathodic reduction of an acid solution of sulphur dioxide with a platinum electrode under the influence of a gradually increasing *E.M.F.* resolves itself into two stages.

In the first stage, from its initial value of + 0·7 volt to + 0·1 volt, a process is operating which results in the separation of sulphur, but only allows a very small current to pass.

In the second stage, which begins in the neighbourhood of

+ 0·2 volt, this process becomes much more intense and has the effect of powerfully depolarising the cathode so that the current density rises rapidly with any further increase in potential. A marked increase in the sulphur separation is also observed.

The explanation of this may be found in the work of Jellinek (*Z. Elektrochem.*, 1911, **17**, 157, 245) on the electrode potential of a mixture of bisulphite and hydrosulphite * ($H_2S_2O_4$), where it is shown that neutral or faintly acid solutions containing the ions of these acids exhibit a well-defined potential which is capable of withstanding considerable polarising currents.

The electrode process may be represented thus :

$$\text{(V.)}\quad 2\,HSO_3' + 2H^{\cdot} = S_2O_4'' + 2H_2O + 2\oplus.$$

It is probable that this electrode equilibrium will tend to establish itself whenever the necessary ions are present, as they are in the solutions we are considering. Hence on placing a platinum electrode in an acid solution of sulphur dioxide and polarising cathodically, the reaction (V) will tend to establish a concentration of hyposulphurous acid corresponding to the potential of that electrode.

We may calculate the concentration of hyposulphurous acid at various potentials from Jellinek's data. The electrode potential, $E_a$, is given by

$$E_a = 0{\cdot}265 - 0{\cdot}029\ \log_{10}[S_2O_4'']/([H^{\cdot}][HSO_3'])^2$$

and the dissociation constant of sulphurous acid.

$$[HSO_3'][H^{\cdot}]/[H_2SO_3] = 1{\cdot}7 \times 10^{-2}.$$

For the present work the concentration of the total sulphur dioxide is 0·1*N* and if we assume that it is present as sulphurous acid we have $[H_2SO_3] = 0{\cdot}1$, whence $[HSO_3'][H^{\cdot}] = 1{\cdot}7 \times 10^{-3}$.

Therefore $\log_{10}[S_2O_4''] = \{(0{\cdot}265 - E_a)/0{\cdot}029\} + \log_{10}(3 \times 10^{-6})$. This equation gives the figures shown in Table III.

TABLE III.

| $E_a$ (volt) | 0·00 | 0·10 | 0·20 | 0·40 | 0·60 | 0·80 |
|---|---|---|---|---|---|---|
| $[S_2O_4'']$ | $5 \times 10^{3}$ | $1{\cdot}5 \times 10^{-1}$ | $5 \times 10^{-4}$ | $10^{-10}$ | $10^{-18}$ | $10^{-25}$ |

The concentrations of $[S_2O_4'']$ in Table III. represent equilibrium values, but hyposulphurous acid is unstable in acid solution and rapidly decomposes, yielding sulphur as follows :

$$\text{(VI.)}\quad 2H_2S_2O_4 = 3SO_2 + S + 2H_2O.$$

The decomposition of hyposulphurous acid may also conceivably proceed indirectly with the formation of thiosulphuric acid or the

* Hyposulphurous acid in this paper signifies Jellinek's "hydrosulphurous" acid.

thionic acids, all of which would ultimately produce sulphur and sulphur dioxide.

At the initial polarisation potentials above 0·2 volt, the current density is regulated by the quantity of hyposulphurous acid decomposing in unit time, and this will be an exceedingly small value, since the total amount of the acid present at any instant is of a small order, as Table III shows.

At + 0·2 volt the equilibrium concentration of the acid has reached measurable magnitude and the current density will increase rapidly, whilst at + 0·1 volt, when $[S_2O_4''] = 1{\cdot}5 \times 10^{-1}$, the current density is limited only by concentration polarisation.

*Mechanism of the Reduction of Sulphur Dioxide by Chemical Means.*

The present work indicates that reduction of sulphur dioxide at the cathode proceeds with the primary formation of hyposulphurous acid, and it is reasonable, therefore, to suppose that reduction by chemical means would follow a similar course.

The primary reaction in the case of a ferrous-ferric mixture is probably similar to that of equation V and may be represented thus:

$$\text{(VII.)}\quad 2Fe^{\cdot\cdot} + 2HSO_3' + 2H^{\cdot} \rightleftharpoons 2Fe^{\cdot\cdot\cdot} + S_2O_4'' + 2H_2O.$$

The amount of hyposulphite present at any instant will be small. Thus the potential of a ferrous-ferric mixture containing 99·5 per cent. of ferrous iron, in concentrated hydrochloric acid solution, is 0·61 volt, hence the concentration of $[S_2O_4'']$ in equilibrium with this mixture in presence of sulphur dioxide is of the order of $10^{-18}$ (see Table III.). Attempts to detect this intermediate compound by qualitative chemical reactions are therefore unlikely to be successful.

It should be noted that there will always be a tendency for the equilibrium value of $[S_2O_4'']$ to be formed, but it is never actually reached owing to the secondary reaction VI, which is continually removing the hyposulphite.

A study of the kinetics of the reaction between sulphur dioxide and ferrous salts in phosphoric acid solution has indicated the reversible formation of an intermediate sulphur compound, X (J., 1923, **123**, 2377, 2388), which in its turn can decompose irreversibly, giving rise to sulphur. In the light of the present work, it will be necessary to regard the intermediate compound X as consisting of more than one substance; for example, the short-lived hyposulphurous acid passes reversibly into a substance of longer life, such as (*a*) a thionic acid or (*b*) an active form of sulphur. The velocity experiments would only be concerned with the longer-lived substance (the thionic acid or active sulphur), but the initial

product, hyposulphurous acid, would be important in deciding the decomposition voltage relations.

The products of the reduction of sulphur dioxide by a number of reagents are shown in Table IV.

TABLE IV.

*Products of the reduction of sulphur dioxide.*

| Conditions. | Product. |
|---|---|
| Aluminium, acid solution. | Hydrogen sulphide. |
| Zinc, faintly acid solution. | Hyposulphurous acid. |
| Titanium chloride, acid solution. | Hydrogen sulphide and hyposulphurous acid. |
| Stannous chloride, acid solution. | Stannous and stannic sulphide, hydrogen sulphide, and hyposulphurous acid. |
| Ferrous chloride. | Sulphur. |
| Cuprous chloride. | Sulphur, copper sulphide. |
| Mercurous chloride. | Sulphur. |
| Tervalent molybdenum, in sulphuric acid. | Sulphur, molybdenum sulphide, tetrathionic acid. |

These products are such as would be expected if the reactions proceed on the lines suggested in this paper. The formation of sulphides by the decomposition of hyposulphites in acid solution is well known. Hyposulphurous acid is actually detected in cases where substances, *e. g.*, zinc, titanous chloride, and stannous chloride exerting strong reducing potentials are present in neutral or only faintly acid solutions.

Tetrathionic acid may be formed from hyposulphurous acid or by the action of nascent sulphur in presence of sulphur dioxide.

*Summary.*

1. The potential of sulphur dioxide in acid solution in presence of sulphur and of the sulphate-ion has been studied at room temperature and found to be inaccessible.

2. Experiments on the cathodic reduction of sulphur dioxide in acid solution show that the direct formation of hydrogen sulphide or of sulphur is unlikely.

3. It is concluded that hyposulphurous acid ($H_2S_2O_4$) is the primary product of the cathodic reduction of sulphur dioxide in acid solution.

4. It is suggested that the primary reaction in the reduction of sulphur dioxide in acid solution by chemical reagents is the reversible formation of hyposulphurous acid in very small concentration. The presence of products such as sulphur, hydrogen sulphide, and thionic acids is to be attributed to secondary reactions of the hyposulphurous acid.

*Addenda.*

Since the completion of this work, an interesting list of reducing potentials has been published by D. F. Smith and J. E. Meyer (*J. Amer. Chem. Soc.*, 1924, **46**, 75), based on an extensive study of the free energy of sulphur compounds by G. N. Lewis and his collaborators.

The following data are of special interest in this connexion :

| | | E°. | $e_{0a}$. |
|---|---|---|---|
| VIII. | $SO_2 + 4H^{\cdot} \rightleftharpoons S + 2H_2O + 4 \oplus$ | −0·470 | +0·747 |
| IX. | $SO_4'' + 4H^{\cdot} \rightleftharpoons SO_2 + 2H_2O + 2 \oplus$ | −0·138 | +0·415 |
| X. | $SO_2 + 6H^{\cdot} \rightleftharpoons H_2S + 2H_2O + 6 \oplus$ | −0·360 | +0·637 |

The reduction potentials are calculated for the molecular quantities in the equations (except in the case of sulphur, which is assumed to be solid) and are referred to the hydrogen electrode as zero. The values under column $e_{0a}$ are obtained from the expression $e_{0a} = 0{\cdot}277 - E°$, and have been inserted to facilitate comparison with the scale used in this paper.

It will be seen that these values are in accordance with the action of sulphur dioxide upon ferrous and ferric salts (compare Table I). Sulphur dioxide, acting as a reducing agent (equation IX), gives $e_{0a} = +\,0{\cdot}414$ volt, which is well below the potential of ferric salts in dilute acid solution.

On the other hand, equation VIII corresponds to a potential of $e_{0a} = 0{\cdot}747$, and this is sufficient to give sulphur dioxide an oxidising character towards ferrous salts in strongly acid solution.

It may also be noted that the reduction of sulphur dioxide to hydrogen sulphide (equation X) could be the primary process as far as the reduction potential $e_{0a} = +\,0{\cdot}637$ is concerned.

We desire to express our thanks to the Department of Scientific and Industrial Research for a grant which enabled one of us (F. J.) to take part in this investigation.

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EDGBASTON.

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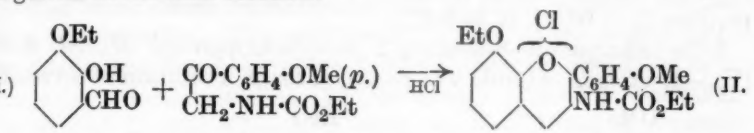
## CCXCVII.—*A New Route to the* 3-*Hydroxybenzopyrylium Salts.*

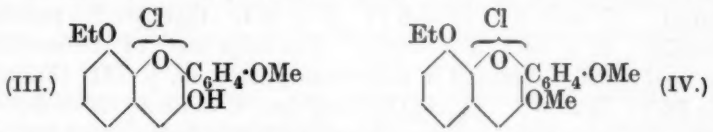
By LESLIE RANDAL RIDGWAY and ROBERT ROBINSON.

IN continuation of efforts to prepare a 3-aminobenzopyrylium derivative the present authors synthesised 3-carbethoxyamino-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium chloride (II) by con-

densation of 2-hydroxy-3-ethoxybenzaldehyde with ω-carbethoxyamino-*p*-methoxyacetophenone (I) by means of hydrogen chloride in glacial acetic acid solution.




This salt was difficult to recrystallise and the crystalline methyl ether of the related pseudo-base was analysed. When heated on the steam-bath with 20 per cent. hydrochloric acid, considerable decomposition occurred and 3-hydroxy-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium chloride (III) crystallised from the solution after cooling. The same salt was obtained by hydrolysis of the product of condensation of 2-hydroxy-3-ethoxybenzaldehyde and ω-acetoxy-*p*-methoxyacetophenone in presence of hydrogen chloride.



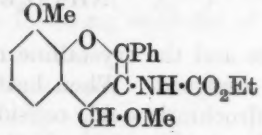

Attempts were made to effect the partial hydrolysis of 3 : 4′-dimethoxy-8-ethoxy-2-phenylbenzopyrylium chloride (IV) with formation of (III), but this was not found to be possible and it is evident that the pyrylium nucleus has full aromatic character. The above results have a bearing on the problem of the synthesis of the partially methylated anthocyanidins, especially those related to delphinidin and possessing a free hydroxyl group in position 3. ω-Acetoxyacetophenone derivatives have not previously been employed in direct condensations to pyrylium salts and the interest of the route through the ω-aminoacetophenones resides in the fact that these substances are accessible from the acetophenones. On the other hand, the conversion of an acetophenone into an ω-hydroxyacetophenone is a formidable operation in any case and a method applicable to polyhydroxyacetophenones or even their acyl derivatives has yet to be discovered.

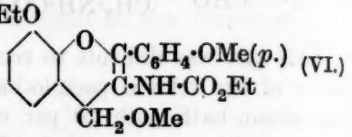
## Experimental.

*Carbethoxyamino*-p-*methoxyacetophenone* (I).—Sodium bicarbonate (12 gms.) and ethyl chloroformate (2·4 gms.) were gradually and alternately added to a cold, mechanically agitated solution of ω-amino-*p*-methoxyacetophenone stannichloride (7 gms.) in water (80 c.c.). After an hour, the solid was collected and extracted with boiling alcohol, and the united filtered extracts were concentrated.

The cooled solution deposited long, glistening, colourless needles, m. p. 76° (2·5 gms.). A further quantity (1·1 gms.) was obtained from the mother-liquors (Found: C = 60·6; H = 6·5. $C_{12}H_{15}O_4N$ requires C = 60·8; H = 6·3%).

*3-Carbethoxyamino-8-methoxy-2-phenylbenzopyranyl Methyl Ether* (V).—Hydrogen chloride was passed through a solution of *o*-vanillin

(V.) 

(VI.)

(1·5 gms.) and ω-carbethoxyaminoacetophenone (2 gms.) in acetic acid (12 c.c.) during 5 hours. Next day, addition of water precipitated a buff solid which was crystallised from methyl alcohol, the solution being boiled during 15 minutes before filtration. After two recrystallisations colourless prisms, m. p. 101°, were obtained (Found: C = 67·8; H = 6·1; N = 4·1. $C_{20}H_{21}O_5N$ requires C = 67·6; H = 5·9; N = 3·9%). The *ethyl ether* of the carbinol was analogously obtained in colourless prisms, m. p. 111° (Found: C = 68·3; H = 6·5. $C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2%). Both substances are unchanged by cold dilute mineral acids, but, on heating, orange-red oxonium salts are produced.

*3-Carbethoxyamino-4′-methoxy-8-ethoxy-2-phenylbenzopyranyl Methyl Ether* (VI).—Dry hydrogen chloride was led through a solution of 2-hydroxy-3-ethoxybenzaldehyde (2·7 gms.) and ω-carbethoxyamino-*p*-methoxyacetophenone (3·9 gms.) in acetic acid (20 c.c.) during 6 hours. The pyrylium chloride (II), separating as a dark red oil on addition of ether, crystallised on scratching, and was then washed with ether, dried (6·4 gms.), and crystallised by adding ligroin to its solution in chloroform saturated by hydrogen chloride. In contact with water, it yields the related pseudo-base, a grey solid which is converted on boiling with methyl alcohol into the *methyl ether* (VI), prisms from methyl alcohol, m. p. 104° (Found: C = 66·3; H = 6·2; N = 3·6. $C_{22}H_{25}O_6N$ requires C = 66·2; H = 6·3; N = 3·5%). In the cold, even concentrated hydrochloric acid does not change this ether in a short period, but, on warming, the characteristic orange-red solution of a pyrylium salt is produced. Hot dilute aqueous sodium hydroxide also dissolves the substance and the yellow solution is at first decolorised on the addition of hydrochloric acid, whilst excess causes the development of a deep orange-red colour, probably as the result of the formation of the pyrylium salt described below.

*3-Hydroxy-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium Chloride* (III).—(A) A mixture of 3-carbethoxyamino-4′-methoxy-8-ethoxy-

2-phenylbenzopyrylium chloride (2 gms.) and 20 per cent. aqueous hydrochloric acid (25 c.c.) was heated on the steam-bath during 2 hours. The filtered solution deposited crystals on cooling, which separated from dilute hydrochloric acid in silky, crimson needles with a purple reflex. The yield from 7·5 gms. of the carbethoxyamino-derivative was only 0·9 gm. The substance was dried in a vacuum and then melted at 176° (decomp.) (Found: C = 63·1, 63·7; H = 5·3, 5·2; Cl = 10·5, 10·3. $C_{18}H_{17}O_4Cl,0·5aq$ requires C = 63·3; H = 5·3; Cl = 10·4%). This salt is sparingly soluble in cold dilute hydrochloric acid to a lemon-yellow solution. It is readily soluble in alcohol and chloroform, giving brownish-yellow and pale orange solutions respectively. It is not affected by cold water but, on heating, the colourless pseudo-base is produced and acidification restores the yellow colour of the oxonium salt. *iso*Amyl alcohol extracts the salt completely from aqueous solution and the extract is immediately decolorised by the addition of sodium acetate. The *bromide* crystallises from dilute hydrobromic acid in slender, red needles, m. p. 197° (decomp.). The *ferrichloride* crystallises from acetic acid in glistening, orange-red plates, m. p. 196°.

(B) Hydrogen chloride was passed through a solution of 2-hydroxy-3-ethoxybenzaldehyde (2 gms.) and ω-acetoxy-*p*-methoxyacetophenone (2 gms.) in anhydrous ether (30 c.c.) during 4½ hours. Next day, 1·7 gms. of orange-red crystals were collected and 0·4 gms. recovered from the mother-liquor by extraction with aqueous hydrochloric acid. The substance was recrystallised from 25 per cent. hydrochloric acid in bright red, silky needles exhibiting a purple glance (Found: C = 63·3; H = 5·4. $C_{18}H_{17}O_4Cl,0·5H_2O$ requires C = 63·3; H = 5·3%). The salt melted at 176° with decomposition and in all its properties was identical with the substance prepared by method (A). The *ferrichloride* had the crystalline form and appearance already described and melted at 196°, alone or mixed with a specimen prepared by method (A) (Found: C = 51·4; H = 4·2; Fe = 6·9.

$$C_{18}H_{17}O_4Cl_4Fe,C_{18}H_{17}O_4Cl,0·5H_2O$$

requires C = 51·6; H = 4·2; Fe = 6·7%). Abnormal ferrichlorides are not frequently encountered, but an instance has been previously recorded (Engels, Perkin, and Robinson, J., 1908, 93, 1151). *iso*Brazilein ferrichloride methyl ether, prepared from dimethylbrazilein, has the composition

$$C_{17}H_{13}O_4Cl_4Fe,C_{17}H_{13}O_4Cl,H_2O.$$

3:4′-*Dimethoxy*-8-*ethoxy*-2-*phenylbenzopyrylium Chloride* (IV).—A solution of 2-hydroxy-3-ethoxybenzaldehyde (1·85 gms.) and ω:4-dimethoxyacetophenone (2 gms.) in dry ether (10 c.c.) was saturated with hydrogen chloride during 90 minutes. The red

crystalline deposit (2·5 gms.) crystallised from dilute hydrochloric acid in red needles, m. p. 160° (decomp.) (Found: C = 55·7; H = 6·3. $C_{19}H_{19}O_4Cl,3·5H_2O$ requires C = 55·7; H = 6·4%). This salt is decomposed by water with the formation of a colourless pseudo-base, from which the oxonium chloride may be readily regenerated. Unsuccessful attempts were made to hydrolyse it so as to produce the 3-hydroxybenzopyrylium derivative described above. The related *bromide*, maroon needles, m. p. 135—138° (decomp.), is unaffected by treatment with aqueous hydrobromic acid (*d* 1·49) during 3 hours at 100.° Demethylation occurred, however, when the salt (1 gm.) was heated at 100° in a sealed tube with acetic acid (10 c.c.) saturated with hydrobromic acid. The *bromide*, isolable after 3·5 hours, occurred in slender, red needles, m. p. 155° (decomp.). Addition of sodium acetate to a solution of this salt gave a red colour base and it was therefore evident that the methoxyl in position 4 had been attacked.

3 : 4′-*Dimethoxy*-8-*ethoxy*-2-*phenylbenzopyrylium ferrichloride* crystallises from acetic acid, in which it is moderately readily soluble, in feathery, glistening, red needles, m. p. 166° (Found: C = 44·6; H = 3·9. $C_{19}H_{19}O_4Cl_4Fe$ requires C = 44·8; H = 3·7%). The solutions of this salt in alcohol and chloroform are yellow and orange, respectively.

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THE UNIVERSITY, MANCHESTER. [*Received, July 11th*, 1924.]

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## CCXCVIII.—*The Dissolution of Substances in Mixed Liquids with Special Reference to Colloids.*

By ERNEST WALTER JOHN MARDLES.

IT has often been observed that a colloidal substance such as a protein or a cellulose ester is much more readily dispersed in a mixture of liquids than in the liquids taken singly, and occasionally non-solvents form a solvent mixture, *e.g.*, cellulose nitrate in ether–alcohol, cellulose acetate in alcohol–nitrobenzene, casein in pyridine–water, gliadin or zein in aqueous alcohol. Again, a "diluent" such as water or alcohol increases the solvent power of acetone for the acetate or nitrate of cellulose when added in the right amount, also the addition of diethylamine, pyridine, etc., allows gelatin to be peptised in water at a much lower temperature, although these

liquids are non-solvents. The marked increase in solvent power produced by the addition of another liquid, not necessarily a solvent, has also been found with some crystalline substances, *e.g.*, cinchonine in chloroform–1% alcohol (Oudemans, J., 1873, **26**, 533) and phloretin in ether–1% water (Schiff, *Annalen*, 1885, **229**, 371).

The composition of the optimum solvent mixture frequently coincides with that of a simple molecular ratio. Usually the position of the maximum to the solvent power–composition curve varies slightly with the conditions, but the number of cases in which the maximum occurs in the close neighbourhood of a simple molecular ratio renders it improbable that the coincidence should be merely a chance occurrence. Below is tabulated a collection of observations illustrating this behaviour; crystalloids have been included in the list.

| Substance. | Optimum solvent mixture or mixture with maximum increase in solvent power beyond the mean value. | Observer. |
|---|---|---|
| Glutin and casein. | 1 mol. pyridine, 2 mols. water. | Levites (*Z. Chem. Ind. Koll.*, 1911, **8**, 4). |
| Zein. | 1 mol. alcohol, 2 mols. water (close proximity). | Galeotti and Giampalmo (*ibid.*, 1908, **3**, 118). |
| Gelatin. | 1 mol. acetic acid, 1 mol. water. | Mardles (*Biochem. J.*, 1924, **18**, 215). |
| Cellulose nitrate. | 1 mol. ether, 1 mol. alcohol. | Stepanow (*Z. ges. Schiess-u. Sprengstoffw.*, 1907, **2**, 43). |
| ,, | 1 mol. toluene, 3 mols. alcohol. | Sproxton (Third Report on Colloid Chemistry). |
| ,, | 1 mol. ether, 1 mol. alcohol (maximum absorption of vapour by nitrocellulose fibrous pulp). | Masson (Report of Discussion on Colloids, by *Far. Soc. and Phys. Soc.*, 1921). |
| Cellulose acetate. | 1 mol. tetrachloroethane, 1 mol. alcohol. | Mardles, Moses, Willstrop (Advisory Comm. for Aeronautics, R. 568). |
| ,, | 2 mols. epichlorohydrin, 1 mol. alcohol. | Mardles (*J. Soc. Chem. Ind.*, 1923, **42**, 127). |
| ,, | 1 mol. epichlorohydrin, 2 mols. acetic acid. | ,, |
| ,, | 1 mol. ethyl formate, 1 mol. acetone. | ,, |
| ,, | 1 mol. mesityl oxide, 1 mol. alcohol. | ,, |
| Mercury chloride. | 1 mol. water, 2 mols. methyl alcohol. | Herz and Anders (*Z. anorg. Chem.*, 1907, **52**, 164). |
| Alkali halides. | 1 mol. alcohol, 3 mols. water. | *Idem* (*ibid.*, 1907, **55**, 271). |
| ,, | 1 mol. glycerol, 4 mols. water | ,, |
| Benzamide. | Maximum at 83% vol. alcohol (3 mols. ethyl alcohol—2 mols. water correspond to 83%). | Holleman and Antusch (*Rec. trav. chim.*, 1894, **13**, 277). |

The view that the molecular complex is the intrinsic solvent has been put forward by Baker (J., 1912, **101**, 1409) in connexion with the dissolution of cellulose nitrate in mixtures of ether and alcohol.

This conclusion was based, not on the simple molecular composition of the best solvent mixture, but on the viscosity of ether–alcohol mixtures and other considerations. He first reviewed the hypothesis that solvent action is due to the unimolecular form of alcohol and found it to be incompatible with many facts.

Barr and Bircumshaw have reasserted the molecular dissociation hypothesis to explain the marked increase of solvent power of acetone for cellulose acetate by the addition of water or alcohol, and suggest that the action of the "diluent" is to increase the amount of unimolecular acetone in the system (Report of Discussion on Colloids, 1921, Far. and Phys. Soc., p. 72). Alcohol, however, cannot be regarded strictly as a diluent, since it is a solvent of cellulose acetate at about 120°, and although there is exceptional increase of solvent power when a binary mixture contains an associated liquid, there are many exceptions. There is, further, no correlation between the degree of association and the enhanced solvent action; thus, ethyl alcohol, benzyl alcohol, nitrobenzene, water, or epichlorohydrin increases the solvent action of acetone for cellulose acetate to a marked extent, whilst with acetic acid the divergence is not large (Mardles, *loc. cit.*). Again, alcohol is much more effective in enhancing the solvent action of an ester, nitrobenzene, etc., for cellulose nitrate or acetate than acetone or acetic acid.

The solvent action of a mixture of liquids is not necessarily wholly attributable to one kind of molecule, simple or associated, but rather to the algebraic sum of the forces exerted on the colloidal particle by all the various molecules and molecular complexes. No theory is complete which does not take into consideration the two important facts that the dissolution of a colloid is preceded by its swelling and that a colloid dispersed in a binary mixture is similar to a ternary mixture of liquids. Knoevenagel and his co-workers, from their extensive researches on the nature of swelling (*Koll. Chem. Beihefte*, 1921, 1922, 1923), have concluded that swelling is in accord with the law of constant combining proportions and is of the nature of a chemical process. It is not surprising that the optimum solvent mixture should sometimes coincide with that of a molecular mixture since the de-association of liquids is also a molecular process.

Holleman and Antusch (1894) considered that the assumption of the existence of alcohol hydrates, although then not definitely proved, would afford a logical explanation of the relatively high solubility of acetamide, alanine, etc., in mixtures of water and alcohol. Recently, further evidence for their existence has been obtained (Cashmore, Dexter, McCombie, and Scarborough, J., 1921, **119**, 970; 1922, **121**, 243, 2308). The viscosity of binary mixtures in relation to the formation of complexes has been widely studied

from the time of Poiseuille and Graham (see, *e.g.*, Dunstan and Thole, J., 1909, **96**, 1556); the more recent work of Bramley (J., 1916, **110**, 10, 434) confirms the general opinion that when the viscosity of a mixture is greater than the mean value it is due to the formation of a molecular complex, and when lower, although the presence of a complex can be proved, the anomaly is due to the molecular dissociation of the liquids.

A number of binary mixtures exhibiting a peak to the viscosity–composition curve, *e.g.*, water and alcohol, formamide and acetic acid, water and pyridine, etc., possess a marked increase in solvent power for colloids beyond the average, whilst the most viscous acetic acid–water mixture is also the best solvent for gelatin, facts in keeping with the view of the superior solvent action of molecular complexes. On the other hand, it is possible from the experimental evidence to establish a diametrically-opposed hypothesis, in that the peptising or solvent action is reduced by complex formation; thus, although aniline and acetic acid are both excellent solvents of cellulose acetate, the mixture 2 mols. acetic acid–1 mol. aniline is an indifferent peptising agent.

The study of the dissolution of colloidal substances in mixed liquids, especially those liquids which contain associated molecules and are known to form molecular compounds on mixing, should lead to an explanation of the characteristic dispersing action of mixed liquids and have an important bearing on the theory of colloidal solution.

*Aniline and Acetic Acid.*—In this mixture two compounds are definitely known to exist, $C_6H_5{\cdot}NH_2,2C_2H_4O_2$, m. p. 16·7°, and $2C_6H_5{\cdot}NH_2,C_2H_4O_2$, m. p. — 19·4° (O'Connor, J., 1921, **119**, 400), the latter being metastable under all conditions. The complex $C_6H_5{\cdot}NH_2,C_2H_4O_2$ apparently does not exist (compare Tizard, J., 1910, **97**, 2493).

The viscosity, surface tension, and stability against precipitation by the addition of a diluent, of sols of cellulose acetate in the mixture have been determined (see Table I and Fig. 1).

Pure, freshly-distilled aniline, $d^{20°}$ 1·0236, and acetic acid, $d^{25}$ 1·0443, were used. The cellulose acetate was kindly supplied gratis by the Société Chimique des Usines du Rhône. The viscosity measurements were made with a set of Ostwald viscosimeters calibrated with water as standard.

From the density data, taken to three places of decimals, it was found that the density–composition curve for the sols was practically parallel to that for the pure liquids.

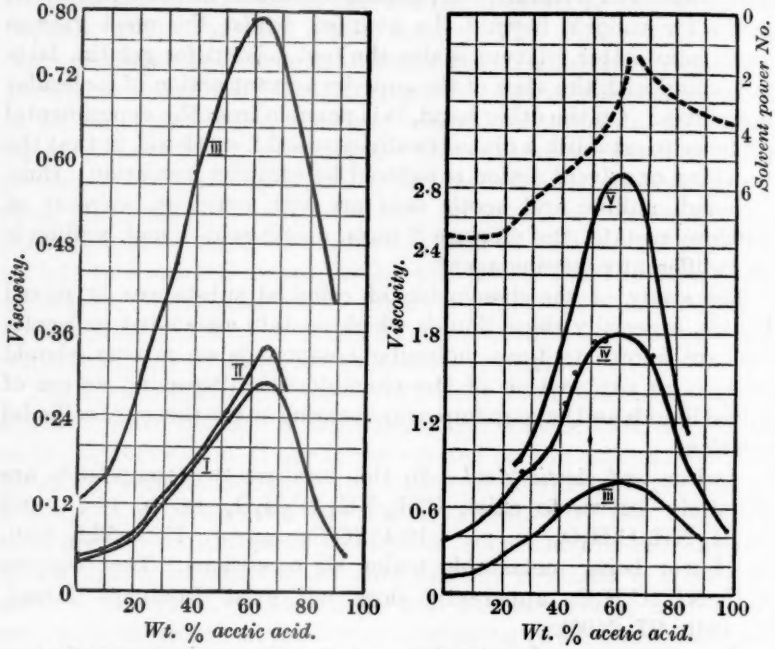
The position of the maximum to the viscosity–composition curve for the pure liquids occurs with a composition richer in acetic acid

than that for the complex 2 mols. acetic acid–1 mol. aniline, but with the addition of the cellulose acetate the difference becomes less. The less stable complex is indicated by a slight bulge.

It will be seen (Fig. 1) that these features are enormously exaggerated with increasing concentration of the colloid, whilst the two portions of the curve forming the peak become sagging. A precisely similar result was obtained with other colloidal systems such as

FIG. 1.

*Viscosity of sols of cellulose acetate in mixtures of aniline and acetic acid.*




I. *Liquids alone.*
II. *Conc.* 0·2 *gm. per* 100 *c.c.*
III. ,, 1 *gm. per* 100 *c.c.*
IV. *Conc.* 2 *gms. per* 100 *c.c.*
V. ,, 3 *gms. per* 100 *c.c.*
*Chained curve—solvent power No.*

gelatin in acetic acid–water mixtures (Mardles, *Biochem. J.*, 1924, **18**, 215).

There is a close similarity in the shape of the viscosity and solvent-power curves, in keeping with the conclusion that the best solvents yield the least viscous sols (Mardles, *J. Soc. Chem. Ind.*, 1923, **42**, 207). The curve relating the surface tension of the sols with composition is slightly sinuous, with excess of aniline the value being a little above the average, and with 20% aniline about 2% lower. These results are in agreement with the view that the presence of a relatively stable complex of the components of the dispersion medium

TABLE I.

Viscosity of sols of cellulose acetate of different concentrations in aniline–acetic acid mixtures at 20°.

$a$ = wt. % of acetic acid in the solvent.
Concentrations are expressed as gms. in 100 c.c.

| Conc. 0 | | 0·2 | | 1 | | 2 | | 3 | |
|---|---|---|---|---|---|---|---|---|---|
| $a$. | $\eta$. | $a$. | $\eta$. | $a$. | $\eta$. | $a$. | $\eta$. | $a$. | $\eta(25°)$. |
| 0 | 0·042 | 0 | 0·052 | 0 | 0·123 | 0 | 0·39 | 25·8 | 0·91 |
| 19·6 | 0·071 | 9·8 | 0·062 | 10·2 | 0·163 | 13·6 | 0·52 | 51·8 | 2·67 |
| 31 | 0·122 | 24 | 0·089 | 20·5 | 0·283 | 23·6 | 0·71 | 60·8 | 2·91 |
| 37·7 | 0·16 | 28·3 | 0·12 | 33·8 | 0·45 | 26·5 | 0·86 | 68 | 2·62 |
| 52 | 0·236 | 33·8 | 0·143 | 39·5 | 0·578 | 31·8 | 0·87 | 82·1 | 1·19 |
| 60 | 0·279 | 51·8 | 0·243 | 50·8 | 0·719 | 36·3 | 1·01 | | |
| 65·5 | 0·287 | 64·5 | 0·335 | 53 | 0·75 | 41·3 | 1·33 | | |
| 70 | 0·275 | 65·5 | 0·339 | 57 | 0·771 | 44·9 | 1·55 | | |
| 84 | 0·115 | 68 | 0·33 | 59 | 0·792 | 51·8 | 1·76 | | |
| 94·5 | 0·05 | 69·2 | 0·318 | 63·3 | 0·785 | 55·5 | 1·76 | | |
| | | | | 67·4 | 0·757 | 71·9 | 1·66 | | |
| | | | | 88·5 | 0·399 | 86·5 | 0·83 | | |
| | | | | | | 97·2 | 0·44 | | |

causes a fall in the degree of dispersion. With regard to viscosity, the colloidal substance acts as a kind of sensitiser, and a small quantity added to a binary mixture exaggerates any divergence or discontinuity on account of the change in the degree of dispersion. With the more dilute sols the effect is not so marked, since dilution favours a higher degree of dispersion, tending towards molecular dispersion under some conditions, and consequently the sols are less sensitive to slight variations in the character of the dispersion medium. The development of any insignificant feature of the viscosity curve can be promoted by increasing the amount of colloid in a binary mixture. This is illustrated by the system benzyl alcohol–*cyclo*hexanone, cellulose acetate again being used.

*Benzyl Alcohol and* cyclo*Hexanone.*—Benzyl alcohol, $d^{25°}$ 1·043, b. p. 205—207°. *cyclo*Hexanone, $d^{25°}$ 0·9423, b. p. 155·5°.

The viscosity of sols of cellulose acetate of different concentrations, their surface tensions, and the temperature of precipitation of the colloid have been determined (Table II and Fig. 2).

The sag in the viscosity–composition curve for the pure liquids develops with increasing concentration of the colloid until it ultimately becomes V-shaped, the shape of the V developing from a bulge in the position corresponding to 1 mol. benzyl alcohol–2 mols. *cyclo*hexanone. The optimum solvent mixture is the least viscous, there being a close correlation between the viscosity and solvent power. The surface tension also of the optimum solvent mixture is lowered less by the cellulose acetate than that of any other mixture, indicating a nearer approach to the condition of true solution.

## Table II.

Viscosity of cellulose acetate sols in mixtures of benzyl alcohol and *cyclo*hexanone at 25°.

*a* = wt. % of *cyclo*hexanone.

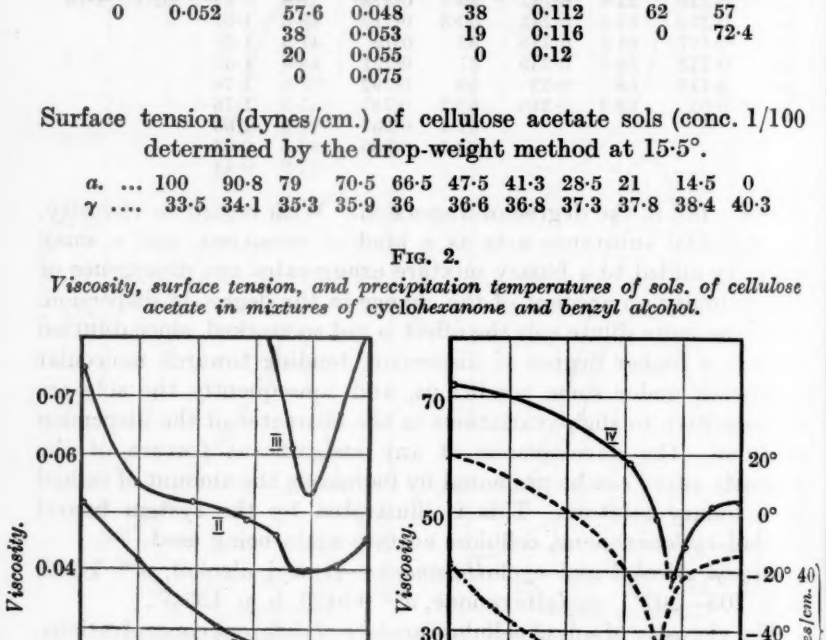
| Conc. 0 | | 0·5 | | 1 | | 10 | |
|---|---|---|---|---|---|---|---|
| *a.* | *η.* | *a.* | *η.* | *a.* | *η.* | *a.* | *η.* |
| 100 | 0·024 | 100 | 0·046 | 100 | 0·082 | 100 | 52·3 |
| 78·3 | 0·025 | 89·8 | 0·041 | 90 | 0·067 | 90 | 51·3 |
| 63·5 | 0·028 | 79 | 0·04 | 80 | 0·053 | 79·8 | 44 |
| 47·5 | 0·031 | 73 | 0·04 | 73 | 0·062 | 77 | 39·4 |
| 20 | 0·042 | 68 | 0·046 | 57·6 | 0·096 | 72 | 49·2 |
| 0 | 0·052 | 57·6 | 0·048 | 38 | 0·112 | 62 | 57 |
| | | 38 | 0·053 | 19 | 0·116 | 0 | 72·4 |
| | | 20 | 0·055 | 0 | 0·12 | | |
| | | 0 | 0·075 | | | | |

Surface tension (dynes/cm.) of cellulose acetate sols (conc. 1/100 determined by the drop-weight method at 15·5°.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *a.* ... | 100 | 90·8 | 79 | 70·5 | 66·5 | 47·5 | 41·3 | 28·5 | 21 | 14·5 | 0 |
| *γ* .... | 33·5 | 34·1 | 35·3 | 35·9 | 36 | 36·6 | 36·8 | 37·3 | 37·8 | 38·4 | 40·3 |

Fig. 2.

*Viscosity, surface tension, and precipitation temperatures of sols. of cellulose acetate in mixtures of* cyclo*hexanone and benzyl alcohol.*




I. *Viscosity of liquids alone.*
II. *Viscosity of sol. conc.* 0·5/100.
III. *Viscosity of sol.* 1/100.
IV. *Viscosity of sol.* 10/100.
– – – – – *Temperatures of precipitation.*
– · – · – · *Surface tension.*

*Mixtures of Acetic Acid with Water and Methyl Alcohol.*—The methyl alcohol was pure; $d^{25°}$ 0·7875. A number of colloidal sub-

stances have been examined, *viz.*, gelatin (Coignet's, ash 1·6%), colophony and orange shellac, cellulose acetate, tannic acid. The solutions of the resins were filtered before viscosity determinations were made and the tannic acid solutions were freshly prepared. The data are included in Table III and Fig. 3.

TABLE III.

Viscosity of solutions in mixtures of acetic acid and methyl alcohol. Concentrations are expressed in gms. in 100 c.c. of dispersion medium.

$b$ = wt. % of methyl alcohol.

| Tannic acid at 25°. Conc. 10. | | | Colophony at 25°. Conc. 10. | | | Shellac at 50°. Conc. 20. | | Cellulose acetate at 25°. Conc. 2. | |
|---|---|---|---|---|---|---|---|---|---|
| $b$. | $d$. | $\eta \times 10^2$. | $b$. | $d$. | $\eta \times 10^2$. | $b$. | $\eta$. | $b$. | $\eta \times 10$. |
| 100 | 0·8412 | 1·02 | 100 | 0·8129 | 0·73 | 100 | 0·13 | 53 | 7·17 |
| 79·4 | 0·8883 | 1·31 | 82 | 0·8575 | 0·94 | 75·5 | 0·16 | 49 | 6·9 |
| 53·3 | 0·9476 | 1·65 | 64 | 0·8954 | 1·16 | 52·5 | 0·21 | 40·5 | 7·84 |
| 34·7 | 0·996 | 1·94 | 43 | 0·9454 | 1·50 | 42 | 0·26 | 30 | 8·21 |
| 28·7 | 1·0114 | 2·07 | | | | 27 | 0·33 | 25 | 8·62 |
| 23·4 | — | 2·23 | | | | 20 | 0·38 | 18·6 | 9·26 |
| 13·2 | 1·0504 | 2·53 | | | | 14·8 | 0·41 | 16·6 | 9·42 |
| 9·2 | — | 2·62 | | | | 7·3 | 0·41 | 8·5 | 9·66 |
| 0 | 1·0826 | 2·67 | | | | 2 | 0·31 | 4·6 | 9·29 |
| | | | | | | 0 | 0·3 | 0 | 9·32 |

Density and viscosity of mixtures of acetic acid and methyl alcohol at 25°.

| $b$ ..... | 0 | 9·24 | 13·16 | 18·6 | 28·7 | 34·7 | 51·6 | 60·2 | 79·1 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| $d$ ..... | 1·0443 | 1·0225 | 1·0118 | 0·9988 | 0·9701 | 0·9540 | | 0·8816 | 0·8383 | 0·7875 |
| $\eta \times 10^2$. | 1·19 | 1·29 | 1·29 | 1·26 | 1·15 | 1·11 | 0·91 | 0·82 | 0·69 | 0·57 |

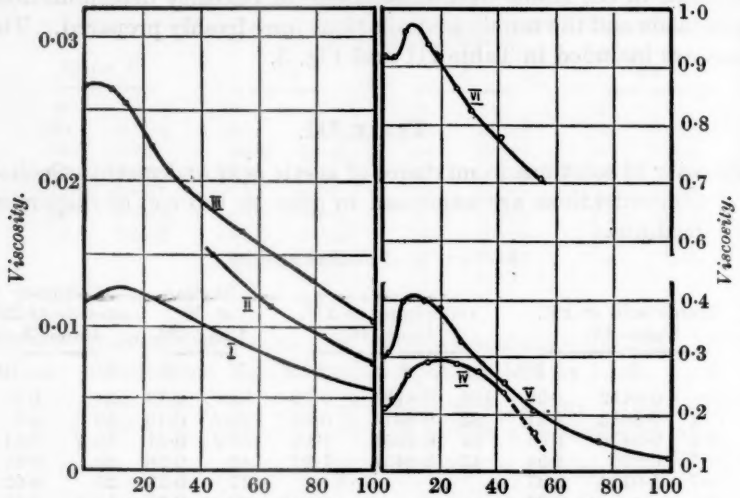
Fig. 3 shows that the viscosity–composition curves for the various colloidal solutions are exaggerated and slightly modified forms of that for the pure liquids, the branches forming the peak having in each case a greater sag. The viscosity data indicate the existence of a complex both in mixtures of acetic acid with methyl alcohol and with water, yet the addition of these liquids, which are non-solvents, to acetic acid increases its solvent action for gelatin or cellulose acetate (Fig. 4).

The effect of the molecular dissociation of the liquids in enhancing solvent action has exceeded the contrary effect due to the formation of complexes of dissimilar molecules.

From the density data given, it will be found that the decrease in volume associated with the formation of the sols is more marked in mixtures with the alcohol in preponderance and reaches a maximum with pure methyl alcohol.

FIG. 3.

*Viscosity of sols of tannic acid, colophony, gelatin, shellac, and cellulose acetate in mixtures of methyl alcohol and acetic acid.*

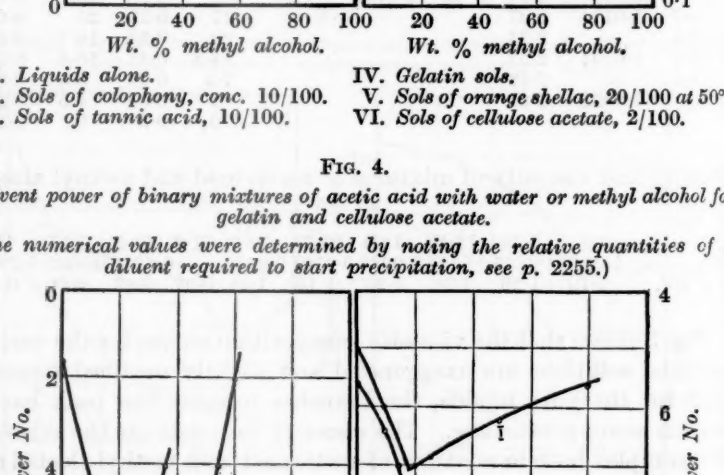



I. *Liquids alone.*
II. *Sols of colophony, conc.* 10/100.
III. *Sols of tannic acid,* 10/100.
IV. *Gelatin sols.*
V. *Sols of orange shellac,* 20/100 *at* 50°.
VI. *Sols of cellulose acetate,* 2/100.

FIG. 4.

*Solvent power of binary mixtures of acetic acid with water or methyl alcohol for gelatin and cellulose acetate.*

(*The numerical values were determined by noting the relative quantities of a diluent required to start precipitation, see p.* 2255.)




I. *Gelatin.*
II. *Cellulose acetate.*

*Ethyl Alcohol and Water.*—Potassium oleate, prepared from "Kahlbaum" oleic acid and alcoholic potassium ethoxide, was not completely soluble in absolute alcohol at 70°, nor in water at 5°, with concentrations of 20 gms. per 100 c.c. On cooling an aqueous solution, concentration 20/100, to about 5°, a very viscous system was obtained which on further cooling set to a thin jelly. A small amount of water increased the solvent action of alcohol considerably, so that with many of the solutions in aqueous alcohol there was apparently no change from the normal sol state until, on cooling below 0°, a faint opalescence was observed (Table IV). Sodium oleate showed a similar behaviour. Further cooling produced a paste or jelly.

TABLE IV.

$a$ = vol. % of alcohol. $b$ = temperature of appearance of a decided opalescence. Conc. 20 gms. per 100 c.c.

| | | | | | |
|---|---|---|---|---|---|
| $a$ ..... | 90 | 76 | 60 | 40 | 20 |
| $b$ for pot. oleate ..... | 1° | −9° | −15·5° | −15° | −10° |
| $b$ for sodium oleate ... | 47° | 8° | 2° | 2° | 8° |

Neither salt dissolved completely in boiling absolute alcohol.

The viscosity data obtained by Bircumshaw (J., 1923, **123**, 91) for sols of potassium oleate in mixtures of water and alcohol show that this salt resembles other colloidal substances in enhancing any feature of the viscosity-composition curve for the pure liquids; thus the development of the sag and the exaggeration of the peak can be traced with the sol of concentration 1/100, and this would account for the initial fall in the viscosity difference recorded by Bircumshaw. The disappearance of the effect in lowering the surface tension of water by potassium oleate with the addition of alcohol is common to gelatin and tannic acid, although with gelatin there is little possibility of any marked change in the colloidal condition.

TABLE V.

The viscosity, $\eta$, of solutions of tannic acid (conc. 10/100) in mixtures of alcohol and water at 25°.

$a$ = wt. % of ethyl alcohol. $b$ = difference of density of solution and solvent.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $a$ ..... | 100 | 87·4 | 60·84 | 50·45 | 32·85 | 21·56 | 10·46 | 0 |
| $b \times 10^4$ ... | 450 | 440 | 373 | — | 342 | — | 320 | 310 |
| $\eta \times 10^3$ ... | 20·4 | 27·4 | 34·3 | 37·1 | 32·4 | 25·1 | 17 | 12 |

Surface tension at 25°.*

| | | | | |
|---|---|---|---|---|
| Conc. ..... | 0 | 1/100 | 2/100 | 10/100 |
| $\gamma$ of ethyl alcohol solns. ..... | 21·79 | 21·8 | 22·2 | 22·83 |
| $\gamma$ of 40·06% „ „ ..... | 30·0] | | | 32·1 |

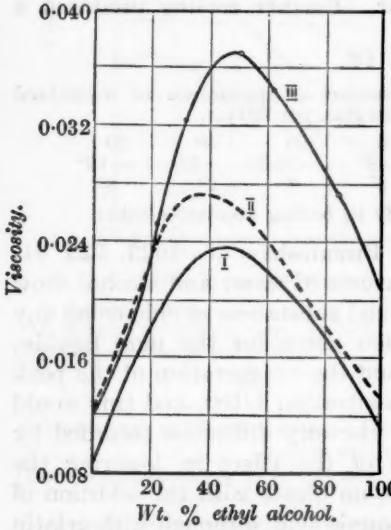
* The surface tensions of the solutions of tannic acid were determined by the maximum bubble-pressure method of Sugden (this vol., p. 27). The hydrosols had a slightly lower surface tension than pure water, the values being variable with time.

Tannic acid is readily dispersed by water and alcohol. The viscosity values of the solutions in the mixed liquids again show the characteristic behaviour of the colloid in enhancing any feature of the viscosity–composition curve for the dispersion mixture (Table V and Fig. 5).

From Fig. 5 it will be seen that tannic acid causes a displacement of the position of the maximum to the viscosity–composition curve towards the alcohol axis, the solution in alcohol being relatively more viscous than the hydrosol. Potassium oleate displaces it in the opposite direction.

FIG. 5.

*Viscosity of sols in mixtures of water and ethyl alcohol.*




I. *Viscosity of pure liquids* (Dunstan, J., 1904, **85**, 817).
II. *Viscosity of sols of potassium oleate* (Bircumshaw, J., 1923, **123**, 91).
III. *Viscosity of sols of tannic acid, conc.* 10/100.

The volume changes reach a maximum with the absolute alcohol, as in the case of potassium oleate, but the abrupt change which occurs at 45 % alcohol in the latter case is less marked with tannic acid.

The mixtures containing a higher proportion of alcohol appear to be the better peptising or dissolving agents for the various colloidal substances mentioned. In the case of benzamide (Holleman and Antusch, *loc. cit.*) and sodium picrate (W. M. Fischer, *Z. physikal. Chem.*, 1918, **92**, 581) the solvent action of the mixture is below or above the average value according as the proportion of alcohol is small or large. Similarly, the peptising action for zein of water containing a little alcohol is considerably less than that of the corresponding mixture of alcohol containing water. Again, the minimum solubility of hydrogen, carbon monoxide, and other gases in water and alcohol occurs with a mixture containing about 28% of ethyl alcohol. The presence of a complex or complexes of water and alcohol is probably responsible for the diminution of the solvent action in each case.

*Aniline with Phenol and o-Chlorophenol.*—In these binary mixtures, the existence of compounds containing equimolecular proportions

of the two components has been demonstrated by Bramley (J., 1916, 109, 10, 434).

The experimental data for cellulose acetate are included in Table VI and Fig. 6.

TABLE VI.

Viscosity of solutions of cellulose acetate in mixtures of aniline and phenol: conc. 2/100.

$a$ = wt. % of phenol.

| $a$. | $\eta^{20°}$. | $\eta^{25°}$. | $\eta^{50°}$. | $a$. | $\eta^{20°}$. | $\eta^{25°}$. | $\eta^{50°}$. |
|---|---|---|---|---|---|---|---|
| 0 | 0·49 | 0·381 | 0·141 | 73·2 | 1·42 | 1·02 | 0·282 |
| 9·6 | — | 0·486 | 0·171 | 75·7 | — | — | 0·258 |
| 20·8 | 0·79 | — | 0·194 | 78·1 | 1·35 | — | 0·255 |
| 30 | 0·96 | 0·704 | 0·207 | 79·5 | 1·3 | 0·97 | — |
| 39·2 | — | 0·855 | 0·241 | 84 | — | — | 0·255 |
| 49·8 | — | 0·959 | 0·264 | 90·2 | — | — | 0·255 |
| 64·7 | — | 1·042 | 0·285 | 96·2 | — | — | 0·259 |
| 71 | — | — | 0·283 | 100 | — | — | 0·259 |

Viscosity and surface tension (dynes/cm.) of solutions of cellulose acetate in mixtures of aniline and *o*-chlorophenol: conc. 2/100.

$a$ = wt. % of *o*-chlorophenol.

| $a$. | $\eta^{20°}$. | $\eta^{40°}$. | $\gamma^{5°}$. | $a$. | $\eta^{20°}$. | $\eta^{40°}$. | $\gamma^{5°}$. |
|---|---|---|---|---|---|---|---|
| 1 | 0·48 | 0·223 | 44 | 64·8 | 1·064 | 0·337 | 43·6 |
| 8 | 0·62 | — | — | 73·7 | 0·95 | 0·313 | — |
| 20 | 0·79 | — | 44·2 | 78·4 | 0·86 | 0·292 | 43·5 |
| 40 | 0·98 | — | — | 91·5 | 0·64 | 0·24 | 43·7 |
| 46·8 | 1·07 | 0·332 | 43·8 | 100 | 0·51 | 0·21 | 43·5 |
| 51 | 1·09 | 0·332 | — | | | | |

Fig. 6 shows once again that the addition of a small proportion of a colloidal substance exaggerates enormously the features of the viscosity–composition curve of the pure liquids. There is a slight sag in the surface tension–composition curve in the neighbourhood of the molecular complex, also the solvent action of the mixtures for cellulose acetate is below the average, but although *o*-chlorophenol is unassociated and has a stronger acid character than phenol, yet there is no evidence that complex formation with aniline has proceeded to a greater extent or that the complex is more firmly held.

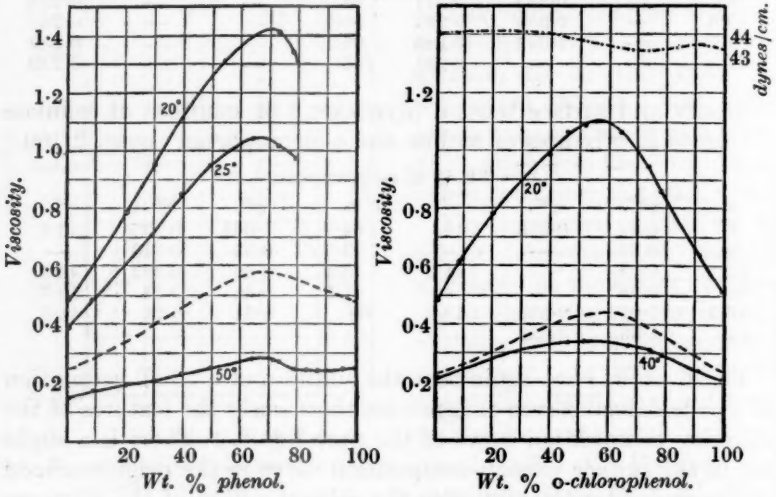
The anomaly is again found with mixtures of aniline and *o*-nitrophenol (Figs. 7—9).

*Solvent Power Numbers.*—The solvent power number is defined as the volume in c.c. of a miscible non-solvent, usually a mixture of xylenes and petroleum spirit, b. p. 90—100°, required to start the precipitation of cellulose acetate from 1 gram of a solution (conc. 5/100) at 20°. The average of a number of readings was taken and the curves were determined by the positions of a large

number of points. In cases where the above-mentioned diluent was not miscible with the solution it was necessary to use ether, and to mixtures containing a solid tending to crystallise the additions were made at a higher temperature, but in order to facilitate comparison the values have all been expressed in terms of one diluent at 20°. Warming was necessary to prepare some solutions, and the cellulose acetate was precipitated on cooling. The temperatures given in the figs. are those at which precipitation occurred. It has been possible to include them in the figs. by noting the additional

FIG. 6.

*Viscosity and surface tension of sols. of cellulose acetate in binary mixtures of aniline with phenol or o-chlorophenol.*




volume of diluent required to start precipitation in the sols when a temperature higher than 20° was taken.

The method of experiment has been described elsewhere (*J. Soc. Chem. Ind.*, 1923, **42**, 127).

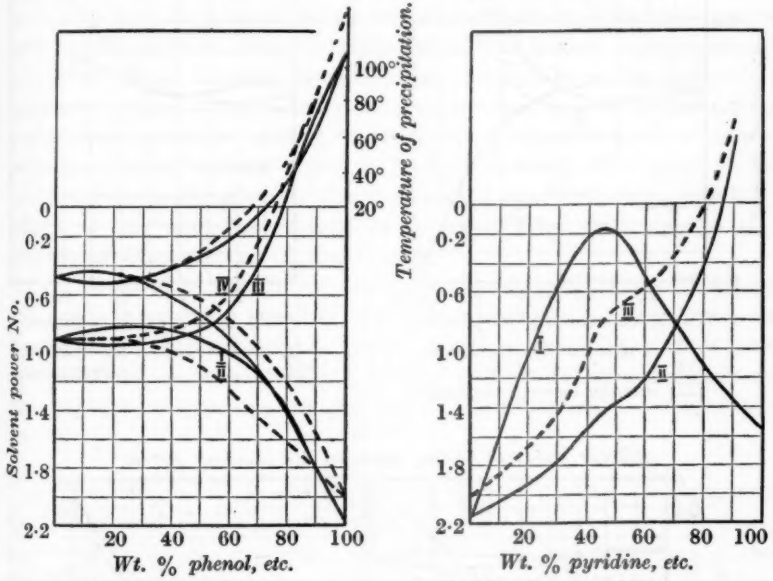
It will be seen from Figs. 7—9 that the peptising action of mixtures of nitrobenzene and its chloro-derivative with aniline or acetone is greater than the average, and in this connexion it is significant that complex formation apparently does not occur in these mixtures (Tinkler, J., 1913, **104**, 2171; Kremann and Rodinis, *Monatsh.*, 1906, **27**, 125). Again, in the mixtures of the nitrophenols with aniline or acetone, the existence of complexes is not indicated by any minimum or diminished peptising action, although breaks in the

curves occur in the neighbourhood of points corresponding to molecular complexes. This result is in accord with the findings of Bramley (*loc. cit.*) and of Philip (J., 1903, **83**, 814).

If the algebraic sum of the divergences from the mean solvent power value of corresponding mixtures of aniline with phenol and nitrobenzene respectively be calculated, the curve drawn therefrom,

FIG. 7.

*The solvent power of binary mixtures for cellulose acetate.*




I. *Aniline and phenol.*
II. *Aniline and* o*-chlorophenol.*
III. *Aniline and nitrobenzene.*
IV. *Aniline and* p*-chloronitrobenzene.*

*(The corresponding curves with acetone are also shown in this figure.)*

I. *Phenol and pyridine.*
II. *Phenol and diphenylamine.*
III. o*-Chlorophenol and diphenylamine.*

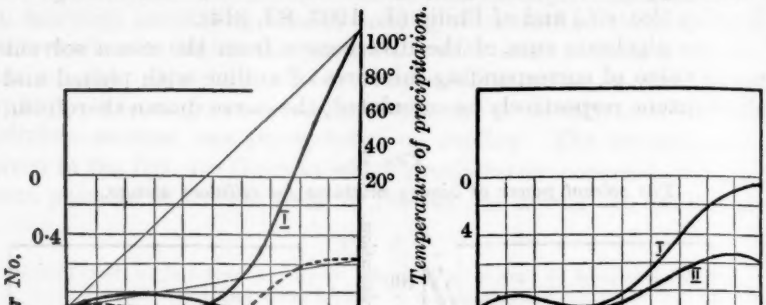
*(The scale of temperatures at which precipitation of the cellulose acetate occurs above 20° corresponds to that of the solvent power numbers.)*

representing the average of the two solvent power curves for the aniline mixtures, bears a striking resemblance to those actually obtained for mixtures of aniline with the nitrophenols (Fig. 8). The same result is found when acetone replaces aniline and for mixtures of phenol with *o*- or *p*-nitroaniline (Fig. 9).

An interesting example of the use of a colloid for the detection of complex formation in a binary mixture is afforded by the mixture phenol–diphenylamine, which, according to freezing-point determinations, etc., does not contain a molecular complex (Bramley;

FIG. 8.

*The solvent power for cellulose acetate of binary mixtures containing aniline*




*Wt. % nitrobenzene (or phenol).*

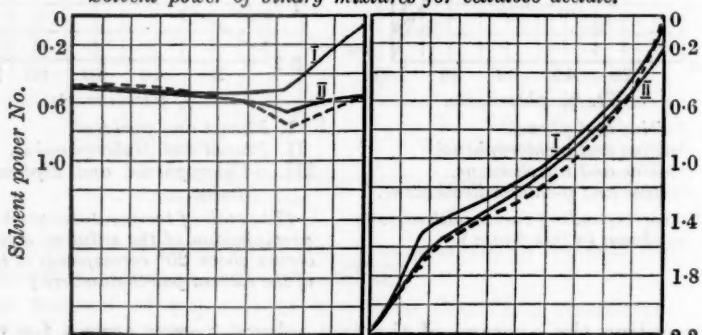
I. *Aniline and nitrobenzene.*
II. „ „ *phenol.*
III. *Average curve (calculated).*

*Wt. % o- or p-nitrophenol.*

I. *Aniline and o-nitrophenol.*
II. „ „ *p-nitrophenol.*

FIG. 9.

*Solvent power of binary mixtures for cellulose acetate.*




*Wt. % o- or p-nitrophenol.*

I. *Acetone and o-nitrophenol.*
II. „ „ *p-nitrophenol.*

*Wt. % p- or o-nitroaniline.*

I. *Phenol and p-nitroaniline.*
II. „ „ *o-nitroaniline.*

– – – – *The average curve calculated from results obtained with binary mixtures containing nitrobenzene, phenol, and aniline (see* Fig. 8).

Philip, *loc. cit.*). A slight bulge in the sagging curve representing the solvent action on cellulose acetate indicates that a complex probably does exist.

*Summary.*

1. A study has been made of the dissolution of a number of colloidal substances, *e.g.*, tannic acid, cellulose acetate, etc., in various binary mixtures of liquids the components of which are known to form or are suspected of forming molecular complexes on mixing. Measurements of the viscosity, surface tension, etc., of the sols have been made.

This characteristic solvent behaviour of mixed liquids cannot be ascribed to the intrinsic action of one kind of molecule or molecular complex, but, in general, whenever molecular simplification occurs in a liquid mixture there is increased solvent action. Any change which tends to increase the molecular complexity of the dispersion medium causes a decrease in solvent action, and therefore when compound formation occurs between the components of a binary mixture loss of solvent power is to be expected. In cases where mixtures containing molecular complexes are good solvents, the effect of the complex formation is masked by that due to the molecular dissociation of the liquids.

2. The use of a colloidal substance in the study of binary mixtures of liquids is rendered possible by the fact that complex formation is frequently indicated by the curve relating peptising action and composition; moreover, the addition of a colloidal substance to the mixture exaggerates any peculiarity of the viscosity–composition curve.

Acknowledgment is made to the Royal Society Government Grant Committee for help towards expenses of the work with non-aqueous colloidal systems. Permission to include some data obtained during researches at the Royal Aircraft Establishment has been given by the Director of Research, Air Ministry.

BIRKBECK COLLEGE, LONDON. [*Received, July 14th*, 1924.]

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## CCXCIX.—*The Carbonates of Ethylene Glycol and Related Compounds.*

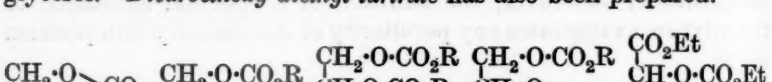
By CHARLES FREDERICK ALLPRESS and WILLIAM MAW.

THE importance of the carbonates and carbonic esters of sugars (Allpress and Haworth, this vol., p. 1223) in connexion with plant metabolism made it desirable to institute a further inquiry into their properties and, to avoid the complexity of the reactions incidental to the sugar group, it was considered that a study of analogous compounds of a simpler type would be profitable. A number of

carbonates and carbonic esters of ethylene glycol and glycerol have therefore been prepared. In addition, partly substituted derivatives of glycerol might conceivably be of considerable value for the synthesis of natural fats.

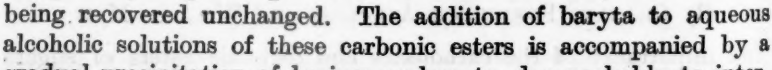
Ethylene carbonate (I) (Nemirowsky, *J. pr. Chem.*, 1883, [ii], **28**, 439) is readily produced in good yield by passing a stream of carbonyl chloride through ethylene glycol at the ordinary temperature and pressure. Glycerol does not appear to react with carbonyl chloride under similar conditions. The same compound is obtainable from ethyl chloroformate and the disodium derivative of ethylene glycol (compare Allpress and Haworth, *loc. cit.*); the presence of dicarbethoxy glycol in the product (Wallach, *Annalen*, 1884, **226**, 82) could not be detected.

*Dicarbomethoxy-* and *dicarbethoxy glycol* (II) have been prepared as colourless liquids from glycol and the corresponding chloroformic ester in presence of pyridine. *Tricarbomethoxy-* and *tricarbethoxy-glycerol* (III) were obtained as viscid liquids by the same method. *Monocarbomethoxy glycerol carbonate* (IV) was isolated by the substitution of dilute alkali for pyridine, and both it and the analogous *monocarbethoxy glycerol carbonate* are produced by the action of the appropriate chloroformic ester upon the sodium derivative of glycerol. *Dicarbethoxy diethyl tartrate* has also been prepared.



(I.) (II.) (III.) (IV.) (V.)

These compounds of ethylene glycol and glycerol containing carbonate and carbonic ester groups are completely hydrolysed by acids, alkalis, and sodium alkoxides, but experiments have been performed with a view to effect partial hydrolysis. By the agency of one molecular proportion of baryta, one carbethoxy-group has been removed as barium carbonate from tricarbethoxy glycerol with formation of *dicarbethoxy glycerol*. In other cases, however, complete hydrolysis of part of the material occurred, the remainder being recovered unchanged. The addition of baryta to aqueous alcoholic solutions of these carbonic esters is accompanied by a gradual precipitation of barium carbonate, due probably to intermediate formation of the barium salts (compare Siegfried and Howwjanz, *Z. physiol. Chem.*, 1909, **59**, 376).



Dilute hydrochloric acid does not appear to be selective in its action on monocarbomethoxy glycerol carbonate. Sodium methyl carbonate is readily produced by treating ethylene carbonate with sodium methoxide.

The interaction of one molecular proportion of ethyl chloroformate and ethylene glycol in presence of pyridine gave ethylene carbonate and not monocarbethoxy glycol as expected. The latter compound, if formed initially, is evidently unstable and loses ethyl alcohol.

$$\begin{matrix} CH_2\cdot OH \\ CH_2\cdot OH \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot O\cdot CO\cdot OEt \\ CH_2\cdot O\cdot H \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot O \\ CH_2\cdot O \end{matrix}\!\!>\!CO.$$

## EXPERIMENTAL.

*Ethylene carbonate* (I) was obtained (yield 65%) (*a*) by passing carbonyl chloride for 8 hours through ethylene glycol, cooled in water.

(*b*) To the disodium derivative of ethylene glycol (prepared from 15·3 gms. of glycol [1 mol.] and 11·1 gms. of sodium [2 mols.]), suspended in dry ether, ethyl chloroformate (78·7 gms. [3 mols.] in ether) was added gradually, and the mixture was heated for 3 hours. The residue after filtration and evaporation gave lower fractions of ethyl chloroformate and ethyl carbonate (Wilm and Wischin, *Annalen*, 1868, **147**, 153), and ethylene carbonate (4·8 gms. after redistillation).

(*c*) Ethyl chloroformate (17·5 gms. [1 mol.] in chloroform) was added gradually to ethylene glycol (10 gms. [1 mol.] in well-cooled pyridine, 12·7 gms. [1 mol.]). The mixture was vigorously shaken for 1½ hours, concentrated under reduced pressure, and the residue treated with water. From the oil extracted with chloroform, 7 gms. of ethylene carbonate were obtained.

Ethylene carbonate and methyl-alcoholic sodium methoxide give a crystalline precipitate of sodium methyl carbonate. After recrystallisation from alcohol, 0·4915 gm. required 5·2 c.c. of 0·9494*N*-hydrochloric acid (calc., 5·3 c.c.).

*Dicarbomethoxy Glycol and Dicarbethoxy Glycol* (II).—Glycol (1 mol.) and pyridine (3 mols.) in chloroform were cooled in ice, the chloroformic ester (3 mols.) in chloroform solution was gradually added, the mixture shaken for 1 hour, the chloroform removed under reduced pressure, and the residue treated with water to remove pyridine and pyridine hydrochloride. The liquid which separated was washed with water till neutral, dried in ethereal solution over anhydrous magnesium sulphate, and distilled after removal of the solvent.

*Dicarbomethoxy glycol* (yield 25%) is a colourless, mobile liquid,

b. p. 101°/3 mm., and is miscible with ether, chloroform, alcohol, benzene, or acetone, but immiscible with water or light petroleum (Found: C = 40·44; H = 5·6. $C_6H_{10}O_6$ requires C = 40·45; H = 5·6%).

*Dicarbethoxy glycol* (yield 66%), b. p. 249—250°/760 mm. (116—117°/2 mm.), is a colourless liquid with a faint but characteristic odour and its solubility is similar to that of dicarbomethoxy glycol (Found: C = 46·15, 46·35; H = 6·5, 6·7; $CO_2$ = 42·5.* $C_8H_{14}O_6$ requires C = 46·60; H = 6·8; $CO_2$ = 42·7%). No trace of decomposition could be detected after boiling dicarbethoxy glycol under reflux for an hour (compare Wallach, *loc. cit.*).

*Partial Hydrolysis of Dicarbomethoxy Glycol and Dicarbethoxy Glycol.*—To dicarbomethoxy glycol, heated in alcoholic solution on a water-bath, exactly 1 mol. of baryta solution was added during 1½ hours. After a further half-hour's refluxing, the liquid was neutral, but carbon dioxide was passed for a few minutes to precipitate any trace of barium. Chloroform extracted a small quantity of ethylene carbonate from the residue after filtration, and concentration under reduced pressure at as low a temperature as possible.

Dicarbethoxy glycol (15·4 gms.) under exactly similar conditions gave 1·6 gms. of glycol, and 3·6 gms. of unchanged substance were recovered (identity established by analysis).

*Monocarbomethoxy Glycerol Carbonate* (IV).—(*a*) To a mixture of 10 gms. of glycerol (1 mol.) in a small quantity of water and 51·5 gms. of methyl chloroformate (5 mols.), 2*N*-caustic soda was added until the solution was just permanently alkaline. The precipitate (4·9 gms.) was crystallised several times from alcohol, *monocarbomethoxy glycerol carbonate* being obtained in colourless needles, m. p. 88° (Found: C = 41·0, 40·4; H = 4·6, 4·5; *M*, in boiling acetone, = 176. $C_6H_8O_6$ requires C = 40·9; H = 4·6%; *M* = 176). It is readily soluble in acetone or hot alcohol, difficultly soluble in ether or benzene, and insoluble in water.

(*b*) Glycerol (12 gms.) and sodium (9 gms.) were heated together on a water-bath for 5 hours with exclusion of moisture, the product was covered with dry ether, methyl chloroformate (49·3 gms. in ether) added gradually, and the mixture boiled for 6 hours. The filtered solution deposited crystals of monocarbomethoxy glycerol carbonate. A further quantity was obtained from the mother-liquors. Yield 6·2 gms.

* About 0·5 gm. of material was heated with excess of standard caustic soda, with exclusion of carbon dioxide, until completely hydrolysed and the sodium carbonate produced was estimated with standard acid using the double indicator method.

An attempt at selective hydrolysis by means of baryta was unsuccessful, the substance being partly unchanged and partly converted into glycerol.

*Monocarbethoxy Glycerol Carbonate* (IV).—Monocarbethoxy glycerol carbonate was prepared in a similar manner to monocarbomethoxy glycerol carbonate (second method above) with the exception that the final ethereal solution was concentrated and the residual liquid fractionated. The main portion distilling at 304—306° as a colourless liquid was *monocarbethoxy glycerol carbonate* (yield = 15%) (Found: C = 43·6, 43·7; H = 5·6, 5·4. $C_7H_{10}O_6$ requires C = 44·2; H = 5·3%).

*Tricarbomethoxy Glycerol and Tricarbethoxy Glycerol* (III).—The procedure for the preparation of these compounds was essentially the same as that for the analogous glycol derivatives except that 4 instead of 3 mols. pyridine and chloroformic ester were used.

*Tricarbomethoxy glycerol* (yield 25%) is a colourless, viscid liquid, b. p. 152°/1·5 mm. It is miscible with the common organic solvents with the exception of light petroleum (Found: C = 40·96; H = 5·2. $C_9H_{14}O_9$ requires C = 40·60; H = 5·3%).

*Tricarbethoxy glycerol* (yield 70%) is a pale yellow, viscid liquid, b. p. 168—169°/0·2 mm., similar in properties to its analogue above (Found: C = 46·61; H = 6·5; $CO_2$ = 43·7; *M*, in boiling acetone, = 323. $C_{12}H_{20}O_9$ requires C = 46·75; H = 6·5; $CO_2$ = 42·9%; *M* = 308).

*Partial Hydrolysis of Tricarbethoxy Glycerol. Dicarbethoxy Glycerol.*—The tricarbethoxy glycerol in hot aqueous alcohol was treated gradually with the quantity of baryta theoretically required for the removal of one ester group as barium carbonate. After filtration, and removal of the solvent, the residual liquid was extracted with ether, and the product fractionated, *dicarbethoxy glycerol*, a colourless, viscid liquid, b. p. 162—163°/0·5 mm., being obtained (Found: C = 45·77, 45·70; H = 6·3, 6·7. $C_9H_{16}O_7$ requires C = 45·76; H = 6·8%).

It was found impossible to remove, either another group from dicarbethoxy glycerol, or two groups from tricarbethoxy glycerol, with baryta, complete degradation resulting in each case.

*Dicarbethoxy Diethyl Tartrate* (V).—Ten grams of freshly distilled diethyl tartrate, 11·6 gms. of pyridine, and 16 gms. of ethyl chloroformate yielded after the usual method of procedure 12·1 gms. of a yellow oil, b. p. 173—174°/0·4 mm., $[\alpha]_D$ + 14·9° (*c* = 3·0 in alcohol) (Found: C = 47·7; H = 6·2; OEt = 46·1. $C_{14}H_{22}O_{10}$ requires C = 48·0; H = 6·3; OEt = 51·4%).

When sodium, 2·2 gms., was substituted for pyridine, the product

amounted to only 1·6 gms. and was optically inactive, b. p. 174—175°/0·6 mm (Found: C = 48·4; H = 6·1%).

The authors wish to thank Professor W. N. Haworth, D.Sc., for the interest he has shown in this work.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-UPON-TYNE. [*Received, July 16th*, 1924.]

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## CCC.—*Condensation of Acetylene and Hydrogen Sulphide in Presence of Catalysts.*

By MARGARET GROSVENOR TOMKINSON.

TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703) states that at about 300° acetylene and hydrogen sulphide, in presence of certain metallic oxides such as aluminium oxide, condense together to give thiophen. He considers that the formation of thiophen from acetylene and iron pyrites at 300° (Steinkopf and Kirchhoff, *Annalen*, 1914, **403**, 1) is due to catalysis, a view which would seem to be supported by the low temperature of the reaction and the large yield compared with that obtained from acetylene and sulphur (V. Meyer and Sandmeyer, *Ber.*, 1883, **16**, 2176). This view, however, was not accepted by Steinkopf, and he and Herold (*Annalen*, 1922, **428**, 123) show that catalytic action can be attributed neither to the iron pyrites itself nor to the impurities it contains, and they further state that ferrous sulphide alone is incapable of promoting the condensation of acetylene at 300°.

Since metallic sulphides act as catalysts in reactions in which sulphur takes part (Sabatier and Mailhe, *Compt. rend.*, 1910, **150**, 1570; Tomkinson, *ibid.*, 1923, **176**, 25), some experiments have been carried out to determine whether this is also true in the case of the reaction between acetylene and hydrogen sulphide. It has been found, as stated by Tschitschibabin, that many metallic oxides catalyse the formation of thiophen in this reaction, but that in every case the oxide is converted into the sulphide with the formation of water. When the sulphide alone is used, the reaction proceeds smoothly, and hence it is the sulphide and not the oxide which functions as the catalyst.

Contrary to the experience of Tschitschibabin, no reaction takes place below 450° with pure alumina, even when the specially reactive alumina of Sabatier is used. Above 450°, decomposition appears to take place with formation of a carbonaceous deposit, and no appreciable quantity of liquid is obtained.

With ferric oxide, ferrous and other metallic sulphides at 300—350°, a considerable quantity of oil is obtained which is apparently identical with that described by Steinkopf and Herold (*loc. cit.*). It seems probable, therefore, that Steinkopf's reaction is catalysed by lower sulphides of iron formed from the pyrites.

## Experimental.

The method employed was that described by Sabatier ("Catalyse en Chimie Organique," 2nd ed., 128), the reaction tube being heated in a Hedley combustion furnace (*J. Soc. Chem. Ind.*, 1923, **42**, 432). There was no difficulty in maintaining a constant temperature, and the difference between the temperature of the sand tray, as registered by a gas-filled mercury thermometer, and that in the reaction tube was approximately constant. Pure hydrogen sulphide was prepared by Fresenius's method (*Z. anal. Chem.*, 1887, **26**, 339) and pure acetylene was obtained from a cylinder of solution from the Birmingham Garage Company, both gases being dried over calcium chloride. The products of reaction were collected in a tube surrounded where necessary by a freezing mixture.

In one experiment using pure ferric oxide in the tube, the gases were passed at the rate of 3 litres of hydrogen sulphide and 6 litres of acetylene per hour, and in the 9 hours after the main production of water had ceased, 30 c.c. of an oily liquid with a garlic-like odour had collected. This liquid on fractional distillation gave :—

(1) A more volatile fraction containing acetaldehyde.

(2) 30 to 40% Thiophen boiling at 81—85°, which was converted into its mercurichloride, according to Volhard (*Annalen*, 1891, **267**, 176). The monomercurichloride melted at 183°.

(3) A less volatile residue, most of which distilled in the neighbourhood of 200°, which was shown by the isatin reaction to contain homologues of thiophen. This liquid underwent some decomposition on boiling and was not further investigated. It probably contained the substances found by Steinkopf in the high-boiling fractions of the products of his reaction (*Annalen, loc. cit.*).

Analysis of the residue in the reaction tube showed a sulphur content of 22%, indicating that a large proportion of the ferric oxide had been transformed into sulphides.

Similar results were obtained with the following substances—where an oxide was used, water was always first produced : ferrous sulphide, nickel oxide and sulphide, cobalt sulphide, cupric oxide and sulphide, vanadium pentoxide and manganese dioxide. A very slight effect only was given by aluminium sulphide and no condensation took place below 450° to 500° in presence of lead monoxide, lead sulphide, silica gel, or alumina—which was not changed to sulphide.

In using molybdenum oxide, $MoO_3$, with hydrogen sulphide and acetylene at 300—400°, a brilliant blue, purple, and red distillate collected in the receiver, but in such small quantity that its examination was a matter of difficulty. The coloured substance does not contain molybdenum, and is given also, although less plentifully, by using in the tube zinc oxide or sulphide, cadmium sulphide, or thoria, none of which is efficacious in promoting the formation of thiophen.

The thanks of the author are due to Professor G. T. Morgan and Mr. C. E. Wood for the interest they have kindly taken in this work.

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EDGBASTON. [*Received, March 11th*, 1924.]

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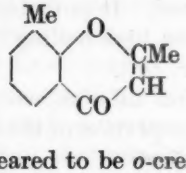
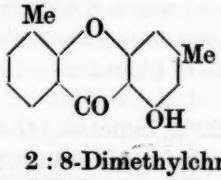
## CCCI.—*The Action of Sodium on the Acetates of* o- *and* p-*Cresol.*

By RICHARD ISAAC EDWARD HALL.

THE action of sodium on phenyl acetate was first studied by Perkin and Hodgkinson (J., 1880, **37**, 487), and further investigated by Perkin (J., 1921, **119**, 1284) and the constitutions of the various products and the mechanism of their formation were discussed. The present communication deals with the action of sodium on *o*- and *p*-tolyl acetates and it is shown that the curious changes observed in the case of phenyl acetate are reproduced in these cases also. In addition to the large amounts of *o*- and *p*-cresol regenerated during the interaction, the substances isolated in the case of *o*-tolyl acetate were 2 : 8-dimethylchromone (I) and 1-hydroxy-3 : 5-dimethylxanthone (II), together with a small quantity only of an acid

(I.)




(II.)

which appeared to be *o*-cresotic acid. 2 : 8-Dimethylchromone had already been prepared by Simonis and Lehmann (*Ber.*, 1914, **47**, 697) from acetoacetic ester by condensation with *o*-cresol, and 1-hydroxy-3 : 5-dimethylxanthone by Kostanecki (*Ber.*, 1894, **27**, 1990), by condensing *o*-cresotic acid with orcinol. In the case of the action of sodium on *p*-tolyl acetate, besides large quantities of *p*-cresol and a very small amount of *p*-cresotic acid ($CO_2H$ : OH : Me = 1 : 2 : 5), the substances isolated were 1-hydroxy-3 : 7-

dimethylxanthone, which had already been obtained by Kostanecki (*loc. cit.*, p. 1989), and 2 : 6-*dimethylchromone*.

The latter substance, which does not appear to have been described, dissolves, like other chromones of this kind, in alcoholic potash to a deep pink solution. The mechanism of the formation of these substances may be explained in exactly the same way as in the case of the analogous substances obtained from phenyl acetate (*loc. cit.*, pp. 1285—1288).

## EXPERIMENTAL.

(i) *Action of Sodium on* o-*Tolyl Acetate*.—During the violent interaction between *o*-tolyl acetate (200 gms.) and sodium (30 gms.), which was conducted exactly as in the case of phenyl acetate (*loc. cit.*, p. 1288), about 25 gms. of an oil distilled which consisted of acetone (*p*-nitrophenylhydrazone test), ethyl acetate, and some *o*-tolyl acetate. The product was mixed with water (1 litre), the oil extracted with ether (A), the brown aqueous layer acidified, and the oil (B) extracted with ether and shaken with dilute ammonia. The ammoniacal extract yielded, on concentrating and acidifying, about 0·3 gm. of an acid which did not melt sharply but had the properties of *o*-cresotic acid, and the mother-liquors of this acid gave, on distillation in steam, much acetic acid.

The ethereal solution (A) was well washed, dried, and the oil carefully fractionated, when, after a large quantity of *o*-cresol had passed over, an oil distilled at about 170—185°/12 mm. and then solidified; it separated from light petroleum in prisms, m. p. 110°, and consisted of 2 : 8-dimethylchromone (I) (Found : C = 75·7; H = 5·8. Calc., C = 75·8; H = 5·7%). The oil (B) contained *o*-cresol, and after this had distilled over, the residue was mixed with a small quantity of high-boiling oil from (A) and carefully fractionated; the fraction, b. p. 225—228°/10 mm., which solidified on stirring with methyl alcohol, separated from this solvent in needles, m. p. 145°, and consisted of 1-hydroxy-3 : 5-dimethylxanthone (II) (Found : C = 75·1; H = 5·2. Calc., C = 75·0; H = 5·0%).

(ii) *Action of Sodium on* p-*Tolyl Acetate*.—This decomposition was carried out exactly as in (i) and yielded acetone, ethyl acetate, acetic acid, and two oils (C) and (D) corresponding with (A) and (B). After the *p*-cresol had been distilled from (C), two main fractions, b. p. 155—160°/10 mm. and 180—240°/15 mm., were obtained. The former crystallised and separated from light petroleum in needles, m. p. 101·5°; this is evidently 2 : 6-*dimethylchromone* (Found : C = 75·9; H = 6·9. $C_{11}H_{10}O_2$ requires C = 75·8; H = 5·7%). The oil (D), after extraction with ammonia, was freed

from *p*-cresol by distillation, the residue mixed with a high fraction from (C), and several times fractionated; the fraction, b. p. 215—220°/12 mm., solidified, and crystallised from alcohol in plates, m. p. 165°, and this substance is evidently 1-hydroxy-3 : 7-dimethylxanthone (Found : C = 75·1; H = 5·1. Calc., C = 75·0; H = 5·0%). The ammoniacal extract of (D) yielded, after decoloration with animal charcoal, concentration, and acidification, an acid (1 gm.), which separated from water in colourless needles, m. p. 150°, and gave a violet coloration with ferric chloride. This acid is clearly *p*-cresotic acid.

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## CCCII.—*The Measurement of the Vapour Pressures of Aqueous Salt Solutions by the Depression of the Freezing Point of Nitrobenzene.*

By NEVIL VINCENT SIDGWICK and ELINOR KATHERINE EWBANK.

SOME time ago it was suggested by one of us (Sidgwick, J., 1920, **117**, 1340) that the vapour pressures of solid hydrates and of aqueous solutions could be measured by means of the lowering which they produced in the freezing point of an organic liquid in contact with them.

The organic liquid must melt sharply, and at a convenient temperature; the depression caused by water must be large enough to admit of accurate measurement, but must not be too large, or the salt may be appreciably soluble in the organic liquid, or the latter in water. The only substance which was found to be satisfactory among some dozen which were examined, was nitrobenzene, in which the depression produced by pure water is 0·51°. When our work on this substance was nearly finished, a paper on the same subject, but dealing only with solid hydrates, was published by Roberts and Bury (J., 1923, **123**, 2037). As our results extend (and on the whole confirm) theirs, and are concerned with solutions, they are described here.

*Preparation of Materials.*—The nitrobenzene was made from benzene which had been frozen out eight times, and freed from thiophen by two treatments with sulphuric acid. To avoid the formation of dinitrobenzene, this was nitrated at 40° by the theoretical amount of nitric acid, in presence of a large excess of sulphuric acid. The nitrobenzene was distilled three times under reduced

pressure at 100° (under atmospheric pressure some decomposition occurs, as is shown by the darkening of the liquid in the distilling flask), and the final fraction was frozen out five times. We find, as do Roberts and Bury, that pure nitrobenzene has a very pale colour, which does not darken on standing even for months, and that it can be left in contact with phosphorus pentoxide for weeks without discoloration.

The sugar used was pure cane-sugar recrystallised with the use of a centrifuge; it left no residue on ignition. The salts were pure laboratory specimens: the calcium chloride was made from pure carbonate.

*Method of Measurement.*—A Beckmann apparatus was used, the thermometer being standardised before each series of readings by taking the "wet" freezing point of the nitrobenzene. Two c.c. of the required solution were then added, stirred with the liquid, and the freezing point was observed. The excess of solution was removed, a fresh portion added, and another reading taken. This process was repeated once or twice more, and the recorded value is in all cases the mean of at least four concordant readings.

The freezing point of pure nitrobenzene was taken in presence of phosphorus pentoxide, the thermometer being standardised by taking the freezing point of specially purified benzene (Sidgwick, *loc. cit.*) under the same conditions. The benzene was assumed to freeze at 5·493° (Richards, Carver, and Schumb, *J. Amer. Chem. Soc.*, 1919, **41**, 2024). The freezing point of dry nitrobenzene was found to be 5·689° (Roberts and Bury 5·669°): in presence of water it freezes at 5·179°, the depression thus being 0·510° (R. and B. 0·511°).

*Relation of the Depression to the Pressure of Water Vapour.*—In order to establish this, it was necessary to use solutions of which the vapour pressures are accurately known, and these are not numerous. For the higher pressures we used solutions of sucrose, for which Berkeley and Hartley (*Phil. Trans.*, 1919, **218**, 295) have determined the ratio of the vapour pressure of the solution to that of pure water at 0° and 30° with great care. The values at these temperatures differ so slightly that we can assume the ratio to be the same at 5° as at 0°. For lower pressures, we used a mixture of sodium sulphate decahydrate and anhydrous salt (Baxter and Lansing, *J. Amer. Chem. Soc.*, 1920, **42**, 419), as did Roberts and Bury, and a saturated solution of calcium chloride hexahydrate (Roozeboom, *Z. physikal. Chem.*, 1889, **4**, 59). The results obtained are given in Table I, together with (in brackets) those of Roberts and Bury for sodium sulphate, and for the systems $SrCl_2,2—6H_2O$, and $H_2C_2O_4,0—2H_2O$, the vapour pressures in these last systems being

from Baxter and Lansing (*loc. cit.*). The observed results are compared with those deduced from the equations

$$d = 0{\cdot}0672p' + 0{\cdot}00148p'^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$d = 0{\cdot}0689p' + 0{\cdot}00130p'^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $d$ = depression of f. p. and $p'$ = pressure of aqueous vapour.

If the results are plotted, it will be seen that our curve, calculated by equation (1), which gives the results within 0·003° in all cases except two, in which there was evidently some error, lies slightly below that of Roberts and Bury, calculated by equation (2).

Roberts and Bury say that this equation "has no theoretical significance," except that it indicates that the water is 15—20% associated in the saturated nitrobenzene solution. But it is significant that this is the precise relation to be expected if (1) the water is present in the nitrobenzene only as single and double

TABLE I.

| | | | Depression. | | | | |
|---|---|---|---|---|---|---|---|
| | | | | Calc. (1). | Calc. (2). | Error × 1000. | |
| Substance. | Wt.%. | $p'$ (mm.). | Obs. | S. & E. | R. & B. | S. & E. | R. & B. |
| Water. | — | 6·625* | 0·510° | 0·510° | 0·513° | ±0° | +3° |
| ,, | | ,, | (0·511) | | | | |
| Sugar soln. | 35·71 | 6·409 | 0·492 | 0·491 | 0·495 | −1 | +3 |
| | 40·70 | 6·345 | 0·485 | 0·486 | 0·489 | +1 | +4 |
| | 45·85 | 6·281 | 0·479 | 0·481 | 0·484 | +2 | +5 |
| | 50·21 | 6·196 | 0·474 | 0·473 | 0·476 | −1 | +2 |
| | 54·43 | 6·101 | 0·466 | 0·463 | 0·469 | −3 | +3 |
| | 60·82 | 5·903 | 0·448 | 0·448 | 0·452 | ±0 | +4 |
| | 65·56 | 5·722 | 0·433 | 0·433 | 0·437 | ±0 | +4 |
| | 70·24 | 5·474 | 0·419 | 0·412 | 0·416 | −7 | −3 |
| $Na_2SO_4$ : 0+10 aq. | | 4·315 | 0·317 | 0·318 | 0·321 | +1 | +3 |
| ,, | | ,, | (0·323) | | | (−5 | −2) |
| $CaCl_2$,6 aq. : sat. soln. | | 2·723 | 0·192 | 0·194 | 0·197 | +2 | +5 |
| $SrCl_2$ : 2+6 aq. | | 1·920 | (0·135) | 0·134 | 0·137 | (−1 | +2) |
| Oxalic acid : 0+2 aq. | | 0·600 | (0·042) | 0·042 | 0·042 | (±0 | ±0) |

* This is the v. p. at 5·179°, which we find to be the f. p. of the wet solvent; Roberts and Bury find 5·158°, and therefore give the v. p. as 6·60 mm., which gives exact agreement between their calculated and observed temperatures at this point.

molecules, and (2) the equilibrium between the two species is that required by the law of mass action: two assumptions which are reasonable, since the concentration of the water is always less than decinormal. For in that case, if $K$ is the association constant, and $c$ the constant for the partition of $H_2O$ between vapour and nitrobenzene,

$$[H_2O] = c \,.\, p' \text{ and } [H_4O_2] = K \,.\, [H_2O]^2 = K \,.\, c^2 \,.\, p'^2.$$

The depression is proportional to the sum of the concentrations of

$H_4O_2$ and $H_2O$, and if $E$ is the cryoscopic constant (for 1 mol. per litre), then

$$d = E.c.p' + E.K.c^2.p'^2,$$

which is the relation given by experiment.

We can also calculate the values of the concentrations, and of the equilibrium constant $K$. If there were no association, the second term of the original equation (1) would vanish, and for $p = 6{\cdot}625$ mm. (the value for water at the f. p. of the wet solvent) the depression would be $6{\cdot}625 \times 0{\cdot}0672 = 0{\cdot}445°$. The actual depression (0·510°) is 0·065° greater, so that $[H_4O_2]/[H_2O] = 65/445 = 0{\cdot}146$. Hence in a saturated solution the concentration of the double molecules of water is 14·6% of that of the single molecules. If, with Roberts and Bury, we take $E = 6{\cdot}87$, then $[H_2O] = 0{\cdot}445/6{\cdot}87 = 0{\cdot}0648N$, and $[H_4O_2] = 0{\cdot}065/6{\cdot}87 = 0{\cdot}0095N$, so that $K = [H_4O_2]/[H_2O]^2 = 0{\cdot}0095/0{\cdot}00420 = 2{\cdot}26$. The saturated solution in nitrobenzene at 5·179° contains 1·50 grams of water per litre. (The corresponding value for benzene is about 0·32.)

These results enable us to determine the vapour pressures of other aqueous solutions. For this purpose, however, equation (1) given above, which expresses $d$ in powers of $p'$, is unsuitable. Further, a correction must be made for the fact (inevitable in a cryoscopic method) that the various solutions are compared at slightly different temperatures. This difficulty is avoided if we consider, instead of $p'$, the vapour pressure of the solution, the ratio of this to that of pure water at the same temperature. This ratio, $p'/p$, is unaffected by small changes of temperature of the order of half a degree. In order to express $p'/p$ in terms of $d$, the depressions corresponding to a series of values of $p'$ were calculated by means of equation (1), and from these, by means of the vapour pressure tables for water, the value of $p'/p$ for each depression, which was plotted against the depression. From the curve so constructed, one can read off the value of $p'/p$ for any observed depression. This curve cannot be exactly expressed by any two-term equation: the nearest is

$$p'/p = 2{\cdot}14\ d - 0{\cdot}35\ d^2 \quad . \ . \ . \ . \ . \ . \quad (3)$$

which agrees within 1%, and for depressions greater than 0·15° within 0·3%. A more accurate form is

$$p'/p = 2{\cdot}164\ d - 0{\cdot}51\ d^2 + 0{\cdot}22\ d^3 \quad . \ . \ . \quad (4)$$

which agrees over the whole range within 1 part in 1000.

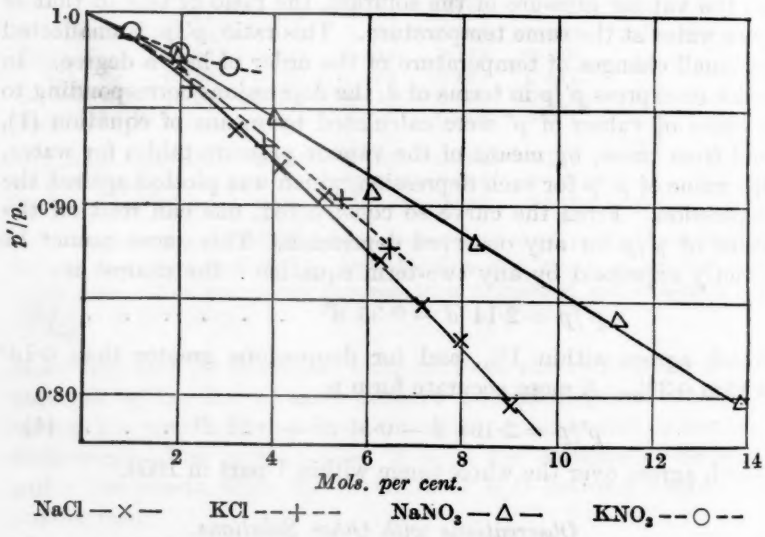
*Observations with Other Solutions.*

The results of these measurements are given in Table II, the concentrations being expressed in molecules of salt to 100 mols.

TABLE II.

| Salt. | Mols. %. | $d$. | $p'/p$ at +5°. S. & E. | $p'/p$ at 100°. Tammann. |
|---|---|---|---|---|
| KCl | 2·26 | 0·491° | 0·966 | 0·959 |
| | 3·80 | 0·472 | 0·931 | 0·931 |
| | 5·44 | 0·457 | 0·904 | 0·903 |
| | 6·44 | 0·443 | 0·878 | 0·878 |
| NaCl | 1·99 | 0·495 | 0·973 | 0·973 |
| | 3·19 | 0·477 | 0·940 | 0·939 |
| | 4·11 | 0·466 | 0·920 | 0·919 |
| | 5·09 | 0·458 | 0·905 | 0·895 |
| | 6·26 | 0·440 | 0·872 | 0·866 |
| | 7·14 | 0·427 | 0·848 | 0·843 |
| | 7·99 | 0·417 | 0·830 | 0·820 |
| | 8·99 | 0·399 | 0·796 | 0·791 |
| $KNO_3$ | 0·953 | 0·505 | 0·991 | 0·986 |
| | 1·945 | 0·499 | 0·980 | 0·971 |
| | 3·03 | 0·495 | 0·973 | 0·956 |
| $NaNO_3$ | 0·858 | 0·505 | 0·991 | 0·986 |
| | 1·94 | 0·497 | 0·978 | 0·967 |
| | 4·03 | 0·480 | 0·945 | 0·929 |
| | 6·04 | 0·459 | 0·907 | 0·892 |
| | 8·24 | 0·444 | 0·880 | 0·853 |
| | 11·27 | 0·423 | 0·841 | 0·799 |
| | 13·87 | 0·400 | 0·798 | 0·760 |
| $CaCl_2$ | 1·93 | 0·478° | 0·942 | 0·943 |
| | 3·03 | 0·447 | 0·885 | 0·916 |
| | 4·11 | 0·416 | 0·828 | 0·843 |
| | 5·45 | 0·359 | 0·721 | 0·761 |
| | 6·79 | 0·313 | 0·634 | 0·684 |
| | 7·81 | 0·261 | 0·534 | 0·605 |
| | 8·57 | 0·232 | 0·477 | 0·561 |
| | 9·17 | 0·192 | 0·398 | 0·528 |
| $K_2SO_4$ | 0·432 | 0·506 | 0·993 | 0·992 |
| | 0·795 | 0·504 | 0·989 | 0·985 |
| $CuSO_4$ | 0·579 | 0·506 | 0·993 | 0·994 |
| | 0·970 | 0·504 | 0·989 | 0·991 |
| | 1·30 | 0·502 | 0·986 | 0·989 |
| | 1·74 | 0·501 | 0·984 | 0·986 |
| $ZnSO_4$ | 1·21 | 0·507 | 0·995 | 0·992 |
| | 2·66 | 0·499 | 0·980 | 0·981 |
| | 4·44 | 0·481 | 0·947 | 0·958 |

FIG. 1.




of solution, and the values of $p'/p$ calculated by equation (4). The values for the four binary salts are plotted on Fig. 1.

Previous measurements of the vapour pressures of solutions of these salts are numerous, but mostly inaccurate. The most satisfactory are those of Smits (*Z. physikal. Chem.*, 1902, **39**, 385; 1908, **51**, 37; sucrose, $KNO_3$,$NaNO_3$,NaCl at 0°; these agree well with our own at 5°) : Tammann (*Mem. Acad. Petersbourg*, 1887, [vii], **35**, no. 9 : NaCl,KCl,$KNO_3$,$NaNO_3$,$CaCl_2$,$ZnSO_4$,$CuSO_4$,$K_2SO_4$ at 100° : he himself rejects his own earlier observations at lower temperatures): Nicol (*Phil. Mag.*, 1886, [v], **22**, 507 : KCl,NaCl,$KNO_3$,$NaNO_3$ at 70—95°) : Roozeboom (*loc. cit.* : $CaCl_2$) : Lincoln and Klein (*J. Physical Chem.*, 1907, **11**, 318 : $KNO_3$,$NaNO_3$ at 25°), and Lovelace, Frazer, and Sease (*Amer. Chem. J.*, 1921, **43**, 102 : KCl at 25°). In Table II, the values obtained by Tammann at 100° (interpolated for the same concentrations) are quoted for comparison; the effect of temperature on the ratio $p'/p$ varies, of course, greatly, depending on the heat of dilution.

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## CCCIII.—*The Hydration of Salts and their Effect on the Vapour Pressure of Water.*

By NEVIL VINCENT SIDGWICK and ELINOR KATHERINE EWBANK.

THE influence of a binary salt on the vapour pressure of water at a given concentration varies greatly with the nature of the salt, as has been shown in the preceding paper. This variation can be studied over a much wider range of salts if we examine the depression of the freezing point of the aqueous solution, which is a direct measure of the lowering of the pressure of water vapour. The effect is most simply expressed by giving the quotient of the depression in degrees by the molecular percentage of salt present. On the van't Hoff formula, this should amount in dilute solution for an undissociated solute to 1·03°, and for a completely dissociated binary salt to 2·06°. We have interpolated the values of the depressions at 3, 6, and 9 mols. per cent. (about 1·7, 3·4, and 5·1 normal) for all inorganic binary salts (including acids and bases) which have been measured up to sufficiently high concentrations, and the quotients of these by the molecular percentages are given in Table I; values in brackets are extrapolated, but never by more than 1 mol. per cent. : in the second column are given the number of molecules of water in the highest known hydrate.

An examination of these figures shows a remarkable regularity. For the nitrates (of which all except the lithium salt are anhydrous),

## TABLE I.

### Values of Depression divided by Mols. per cent.

| Salt. | Water of cryst. | Mols. per cent. 3. | 6. | 9. | References. |
|---|---|---|---|---|---|
| $LiNO_3$ | 3 | 1·33 | 1·55 | 1·58 | 13 |
| $NaNO_3$ | 0 | — | 1·52 | 1·49 | 1 |
| $KNO_3$ | 0 | (1·11) | — | — | 21, 22 |
| $RbNO_3$ | 0 | (1·24) | — | — | 23 |
| $NH_4NO_3$ | 0 | 1·58 | 1·39 | 1·30 | 1 |
| $AgNO_3$ | 0 | 1·19 | 1·03 | (0·82) | 2, 3 |
| $NaNO_2$ | 0 | 1·63 | 1·33 | 1·23 | 14, 15 |
| $KNO_2$ | 0 | 1·06 | 1·20 | 1·24 | ,, |
| KCl | 0 | 1·85 | (1·92) | — | 1 |
| KBr | 0 | 1·88 | 1·93 | — | ,, |
| KI | 0 | 2·02 | 2·05 | 2·12 | 5, 6 |
| KCNS | 0 | 1·80 | 1·83 | 1·84 | 2, 7 |
| CsI | 0 | (1·52) | — | — | 4 |
| $NH_4Cl$ | 0 | 1·88 | 1·98 | — | 1 |
| $NH_4Br$ | 0 | 1·91 | 2·00 | (2·22) | 8 |
| $NH_4I$ | 0 | 1·74 | 1·83 | 1·91 | 9 |
| $NH_4CNS$ | 0 | 1·81 | 1·82 | 1·81 | 2, 7 |
| $K(C_2H_5)SO_4$ | 0 | 1·83 | 1·80 | — | 20 |
| LiOH | 1 | 1·76 | 1·94 | — | 10 |
| NaOH | 7 | 1·98 | 2·35 | 2·84 | ,, |
| KOH | 4 | 2·16 | 2·81 | 3·64 | ,, |
| LiCl | 2 | 2·45 | 3·11 | — | 1 |
| LiBr | 2 | 2·77 | 3·80 | 4·72 | 12 |
| LiI | 3 | 2·76 | 3·83 | 5·19 | ,, |
| $LiNO_2$ | 2 | 1·70 | 2·09 | 2·37 | 14 |
| NaCl | 2 | 1·96 | 2·18 | (2·52) | 1 |
| NaBr | 4 | 2·15 | 2·42 | 2·58 | 8, 11 |
| NaI | 5 | 2·25 | 3·04 | — | 11 |
| HCl | 3 | 2·41 | 3·12 | 4·09 | 17, 18 |
| HBr | 4 | 2·69 | 3·61 | 4·68 | 16 |
| HI | 4 | 2·79 | 3·86 | 5·23 | 18 |
| $HClO_4$ | 3·5 | 2·25 | 2·68 | 3·82 | 19 |
| $HNO_3$ | 3 | 2·16 | 2·38 | 2·74 | 24 |

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the quotients are exceptionally low. This points to association of the anion in the stronger solutions, of which there are other indica-

tions (compare nitric acid). The remaining salts can be divided sharply into two classes, those which form solid hydrates and those which do not. The former invariably give a greater depression than any of the latter. The only exception is lithium hydroxide, where we may suspect experimental error. For example, at 6 mols. per cent. the highest value for an anhydrous salt is 2·05 (KI), and the lowest for a hydrated salt 2·09 ($LiNO_2$: but, as the values for $NaNO_2$ and $KNO_2$ show, the nitrites seem to share the tendency of the nitrates to polymerisation), and the next lowest 2·18(NaCl). Excluding the acids (as not wholly comparable) and the nitrates, the mean values at 3, 6, and 9 mols. per cent. are, for salts forming no hydrates, 1·82, 1·91, and 1·98, and for salts forming hydrates, 2·19, 2·76, and 3·29.

It seems improbable that these differences can be due to any large extent to differences in dissociation, as we are concerned only with the binary salts of strong acids and bases; and when we find the effect related in this way to the power of forming hydrates, it is difficult to resist the conclusion that the result is due to hydration (either of the undissociated or of the dissociated salt or both) removing water from the system and so lowering the vapour pressure and the freezing point. The exact correspondence between this effect and the formation of solid hydrates is remarkable; we might expect some salts to form hydrates in solution which yet would be too soluble to separate as solids; but it seems that this is not so.

It should be mentioned that these regularities are not observed in the alkaline salts of (weak) organic acids (formates and acetates: Sidgwick and Gentle, J., 1922, **121**, 1839; benzoates and hydroxybenzoates, Sidgwick and Ewbank, *ibid.*, 1844). The values for these salts are affected both by the anion and by the cation; but no general difference between hydrated and non-hydrated salts can be detected.

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## CCCIV.—*A Convenient Method for the Preparation of Arsinic Acids from the Corresponding Chloroarsines.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

THE action of sodium toluene-*p*-sulphonchloroamide (chloramine T) on alkyl sulphides and on tertiary arsines has been shown by Mann and Pope to lead to the formation of "sulphilimines" and "arsylimines," respectively (J., 1922, **121**, 1052, 1754). We have found that the action of chloramine T on tertiary chloroarsines affords a

convenient method for the preparation of the corresponding arsinic acids.

The advantage of this method over that described by Wieland and Rheinheimer (*Annalen*, 1921, **423**, 1) for the preparation of phenarsazinic acid is, that no colouring matter is formed during the oxidation, as is the case when hydrogen peroxide is employed. The troublesome separation of the sodium salt of the arsinic acid from sodium chloride or bromide in the method used by Quick and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 805) is entirely avoided.

## Experimental.

The chloroarsine to be oxidised (1 mol.) is dissolved, or suspended in cold acetone (20 c.c. per 1 gm. of substance), and treated with a 10% solution of chloramine T (2 mols.) in cold water. The mixture becomes warm, any colour in the solution disappears, and reaction is complete after boiling for 30 minutes under a reflux condenser. The acetone is distilled off and the *p*-toluenesulphonamide separated by filtration of the cold solution. If the arsinic acid is insoluble in water, or only soluble to a slight extent, it separates with the sulphonamide and is easily obtained by extracting the solid mixture with cold sodium carbonate solution, precipitating with acid, and crystallisation from an appropriate solvent.

If the acid is soluble in water, or only separates from the aqueous mother-liquor on standing, the solution is evaporated to dryness. Extraction of the acid is effected in the same manner as before.

n-*Butylarsinic acid*, soluble in water, m. p. 160°, was prepared from *n*-butylchloroarsine. The yield was 74% of the theoretical (compare Quick and Adams, *loc. cit.*).

o-*Tolylarsinic acid*, $C_6H_4Me{\cdot}AsO(OH)_2$, was obtained in long, colourless needles, m. p. 163—164°, by crystallisation from water. The yield was quantitative (Found: As=34·6. $C_7H_9O_3As$ requires As=34·7%).

*Diphenylarsinic acid* was obtained in a 75% yield from diphenylarsenious chloride. It melted at 169—170° without further purification.

*Phenarsazinic acid* separated from the cold mixture of 10-chloro-5 : 10-dihydrophenarsazine and chloramine T in small needles; yield 92% (Found: As=27·2. $C_{12}H_{10}O_2NAs$ requires As=27·25%).

Wieland and Rheinheimer (*loc. cit.*) showed that phenarsazinic acid forms salts with bases and described the substance as crystallising from glacial acetic acid with 1 mol. of acetic acid. This compound is probably the acetate, and the following salts of phenarsazinic acid have been prepared and demonstrate the amphoteric nature of the parent acid.

*Hydrochloride*, $NH(C_6H_4)_2AsO{\cdot}OH,HCl$.—A hot alcoholic hydrochloric acid solution of phenarsazinic acid was allowed to cool after excess of hydrochloric acid had been added. The hydrochloride crystallised in colourless needles, m. p. 200—205° (decomp.). This salt is useful for characterising phenarsazinic acid (Found: As= 24·3; Cl=11·4. $C_{12}H_{11}O_2NClAs$ requires As=24·06; Cl=11·38%).

*Nitrate*, $NH(C_6H_4)_2AsO{\cdot}OH,HNO_3$.—A suspension of phenarsazinic acid (2·7 gms.) in acetone (10 c.c.) was treated with concentrated nitric acid (2 c.c.), added drop by drop. Solution was then effected by adding alcohol (10 c.c.) and warming. Addition of a 10% solution of hot nitric acid caused the nitrate to be precipitated. On crystallisation from a hot dilute nitric acid–alcohol mixture it was obtained in pale yellow needles which have no definite melting point (Found: As=21·8. $C_{12}H_{11}O_5N_2As$ requires As=22·17%).

*Sulphate*, $[NH(C_6H_4)_2AsO{\cdot}OH]_2,H_2SO_4$.—Phenarsazinic acid was added to a boiling mixture of alcohol (10 c.c.), benzene (10 c.c.), and concentrated sulphuric acid (1 c.c.). After saturation, the solution was filtered, and, on cooling, the sulphate separated in colourless prisms, m. p. 138—140° (decomp.) (Found: As=22·6. $C_{24}H_{22}O_8N_2SAs_2$ requires As=23·12%).

N-*Acetylphenarsazinic acid*, $CH_3{\cdot}CO{\cdot}N(C_6H_4)_2AsO{\cdot}OH$, was obtained in theoretical yield from 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine.* It is insoluble in water, and by recrystallisation from aqueous alcohol is obtained in colourless, flat prisms, m. p. 244—245° (decomp.), containing two molecules of water of crystallisation (Found: $H_2O$=10·43. As, in anhydrous material, =23·5. $C_{14}H_{12}O_3NAs,2H_2O$ requires $H_2O$=10·2. $C_{14}H_{12}O_3NAs$ requires As =23·64%).

N-*Propionylphenarsazinic acid*, $C_2H_5{\cdot}CO{\cdot}N(C_6H_4)_2AsO{\cdot}OH$, prepared from 10-chloro-5-propionyl-5 : 10-dihydrophenarsazine,† was

* (1) 10-*Chloro-5-acetyl-5 : 10-dihydrophenarsazine*, $CH_3{\cdot}CO{\cdot}N(C_6H_4)_2AsCl$, has not been previously described. It is prepared by boiling an excess of acetyl chloride, diluted with dry benzene, with 10-chloro-5 : 10-dihydrophenarsazine for 4 hours. The substance crystallises on cooling and is obtained in small, colourless needles, m. p. 229—230°, on recrystallisation from benzene (Found: As = 23·2; Cl = 11·5. $C_{14}H_{11}ONClAs$ requires As = 23·46; Cl = 11·1%).

† 10-*Chloro-5-propionyl-5 : 10-dihydrophenarsazine*, $C_2H_5{\cdot}CO{\cdot}N(C_6H_4)_2AsCl$, described for the first time, is more difficult to obtain. Preparation is accomplished by boiling 10-chloro-5 : 10-dihydrophenarsazine with a large excess of propionic anhydride, and a small amount of pyridine, diluted with dry xylene, for 10 hours. After removal of most of the xylene the substance crystallises. Recrystallised from benzene–petrol, it separates in colourless plates, m. p. 135—136° (Found: As = 22·4. $C_{15}H_{13}ONClAs$ requires As = 22·48%).

isolated by allowing the mother-liquors, after separation of the *p*-toluenesulphonamide, to stand for 12 hours. The acid was filtered off and washed with successive quantities of hot alcohol (yield 40%). Propionylphenarsazinic acid is insoluble in water or alcohol and melts at 232° (decomp.) (Found: As=22·4. $C_{15}H_{14}O_3NAs$ requires As=22·65%).

N-*Benzoylphenarsazinic acid*, $C_6H_5\cdot CO\cdot N(C_6H_4)_2AsO\cdot OH$, separated from the mixture of 10-chloro-5-benzoyl-5 : 10-dihydrophenarsazine * and chloramine T after standing for some time (yield almost theoretical). The acid crystallises in colourless prisms, m. p. 250° (decomp.) (Found: As=19·35. $C_{19}H_{14}O_3NAs$ requires As=19·77%).

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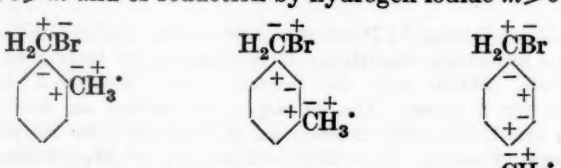
## CCCV.—*Polarity Effects in the Isomeric ω-Bromoxylenes and Isomeric Iodotoluenes.*

By JOHN BALDWIN SHOESMITH and ROBERT HENRY SLATER.

THE investigations of this series (Lapworth and Shoesmith, J., 1922, **121**, 1392; Shoesmith, J., 1923, **123**, 2838; Shoesmith, Hetherington, and Slater, this vol., p. 1312), which have so far been confined to the influence which oxygen exerts as a "key-atom" on halogen atoms in various benzenoid compounds, have been extended and the influence of the hydrogen atoms in a methyl group in such compounds ascertained.

By the same methods as were employed in the first investigations, it has now been possible to show that the isomeric ω-bromoxylenes react in an anticipated order. The order of ease of hydrolysis should be *p* and *o*>*m* and of reduction by hydrogen iodide *m*>*o* and *p*.



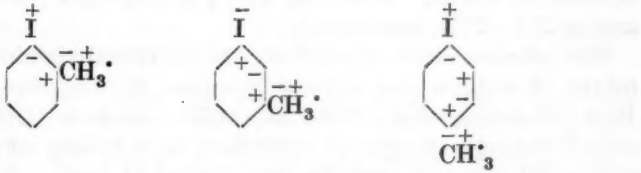
* 10-*Chloro-5-benzoyl-5* : 10-*dihydrophenarsazine*, $C_6H_5\cdot CO\cdot N(C_6H_4)_2AsCl$, has not been previously described. It is prepared from 10-chloro-5 : 10-dihydrophenarsazine in an excess of boiling benzoyl chloride, diluted with dry xylene, for 10 hours. After removal of excess xylene the dark coloured viscous oil is allowed to stand for 2 days and the solid material filtered off. The substance is obtained in colourless, hard crystals, m. p. 180—181° on crystallisation from benzene (Found: As = 19·7. $C_{19}H_{13}ONClAs$ requires As = 19·64%).

Experiment has fully borne out this prediction. It has, in fact, been found that under conditions by which ω-bromo-*m*-xylene is almost quantitatively reduced by hydrogen iodide to *m*-xylene, the isomeric ω-bromo-*p*-xylene is converted into ω-iodo-*p*-xylene.

The complete order of hydrolysis is $p>o>m$, and of reduction $m>o>p$.

The general polar influence exerted by the methyl group is quite marked and all the ω-bromoxylenes are more easily hydrolysed than the unsubstituted benzyl bromide. It must also be pointed out that the meta- and ortho-isomerides are more reactive than the unsubstituted compound to both reagents. As expected, ω-bromo-*p*-xylene is more easily hydrolysed than ω-iodo-*p*-xylene.

The order of ease of reduction of the iodotoluenes, in which the halogens are one place nearer to the "key-atom" than those present in the ω-bromoxylenes, was again as expected, namely, *o* and $p>m$, the reverse of the previous order, except that the ortho-isomeride is the isomeride most easily reduced to toluene.



The meta-isomeride is reduced very slowly under the experimental conditions, and therefore this series differs slightly from that of the halogenated phenols, in which the meta-isomeride is not reduced.

The possibility of the formation of reactive molecules of quinonoid type in any of the compounds here investigated is remote and the two series of experiments are of importance by reason of their simplicity.

It must be pointed out that the suggestion put forward by Lowry (J., 1923, **123**, 824) that the induced alternate influence is only capable of being transmitted when the series is perfectly conjugated is definitely negatived by the different orders of reactivity displayed by the ω-bromoxylenes under the conditions described in the present communication. It must be emphasised, however, that the benzene ring is certainly a very efficient transmitter and possibly even an amplifier of induced polarity effects. In all probability, however, similar effects will not be observed in aliphatic compounds which contain a series of consecutive single bonds. This has recently been stressed by Lapworth (*Far. Soc. Disc.*, 1923, p. 505).

In addition, it is obvious that the tautomeric hydrogen hypothesis

of Thorpe (J., 1911, **99**, 2185, and onwards) cannot be extended to embrace the observations on the differences of ease of reducibility of the methoxybenzyl bromides (Lapworth and Shoesmith, *loc. cit.*) or of the halogen compounds described in the present communication.

## EXPERIMENTAL.

*Preparation of the ω-Bromoxylenes.*—These were all obtained by a general method summarised as follows :—

$$\underset{\text{(I.)}}{CH_3\cdot C_6H_4\cdot NH_2} \longrightarrow \underset{\text{(II.)}}{CH_3\cdot C_6H_4\cdot CN} \xrightarrow[\text{alcohol}]{\text{Na in}} \underset{\text{(III.)}}{CH_3\cdot C_6H_4\cdot CH_2\cdot NH_2} \xrightarrow{HNO_2} \underset{\text{(IV.)}}{CH_3\cdot C_6H_4\cdot CH_2\cdot OH} \xleftarrow[\text{dry benzene}]{\text{HBr in}} \underset{\text{(V.)}}{CH_3\cdot C_6H_4\cdot CH_2Br}$$

The toluidines (I) were converted into the corresponding toluonitriles (II) in the usual manner, and the latter purified by distillation in steam. They had b. p., *o*- 202—204°, *m*- 210—212°, and *p*- 215—217°, respectively.

The nitriles were reduced to the tolylmethylamines (III) by means of sodium and alcohol (compare Kröber, *Ber.*, 1890, **23**, 1026; Sommer, *ibid.*, 1900, **33**, 1073). Sodium (100 gms.) was added, through an upright condenser, to a boiling solution of the nitrile (30 gms.) in perfectly dry alcohol (1 litre). When all the sodium had dissolved, the reduction mixture was diluted with water, acidified with hydrochloric acid, and the alcohol distilled in steam. The tolylmethylamine liberated from the residual acid solution by sodium hydroxide was distilled in steam, extracted from the distillate with ether, dried over sodium sulphate, and purified by distillation.

The yields of the *o*-, *m*-, and *p*-tolylmethylamines obtained by this general method were, *o*- 50%, *m*- 30%, and *p*- 60% of the expected quantity. They distilled at 200—202°, 198—200°, and 194—196°, respectively.

The corresponding tolylcarbinols (IV) were obtained from the amines by the addition of twice the necessary quantity of sodium nitrite to a solution of the base in an excess of dilute hydrochloric acid. Nitrogen was evolved at once. After 12 hours, the reaction was completed on the water-bath. The carbinol, removed from the reaction mixture with ether, was distilled in steam, and obtained pure from the ethereal extract of the distillate. The yields were *o*- 50%, *m*- 70%, and *p*- 40%. *o*-Tolylcarbinol, m. p. 33°, b. p. 112—114°/9 mm.; *m*-tolylcarbinol, b. p. 108—111°/10 mm.; *p*-tolylcarbinol, m. p. 60°. The poor yields of the ortho- and para-

isomerides are due to the fact that appreciable resinification took place during steam distillation of the tolylcarbinols.

The isomeric ω-bromoxylenes (V) were obtained from the corresponding tolylcarbinols by the usual method of saturating the dry benzene solution of the latter with dry hydrogen bromide. The *o*-isomeride, b. p. 102°/11 mm., m. p. 20°; *m*-, b. p. 97—99°/8 mm.; *p*-, b. p. 100°/9 mm., m. p. 35·5°.

*Hydrolysis of the ω-Bromoxylenes at 60°.*

The isomerides were hydrolysed at the temperature of the vapour of boiling chloroform, since this was found to be the most satisfactory temperature at which a series of results could be obtained. The method was that used in a previous communication (Shoesmith, Hetherington, and Slater, *loc. cit.*). The results are summarised in Table I,* where *t*, *w*, and *x* represent time in hours from commencement of experiment, weight of compound used, and percentage changed, respectively.

TABLE I.

| | Ortho-compound. | | Meta-compound. | | Para-compound. | | Benzyl bromide. | | ω-Iodo-*p*-xylene. | |
|---|---|---|---|---|---|---|---|---|---|---|
| *t.* | *w.* | *x.* | *w.* | *x.* | *w.* | *x.* | *w.* | *x.* | *w.* | *x.* |
| ½ | 0·1060 | 55 | 0·0980 | 25 | 0·0983 | 66 | 0·1093 | 22 | 0·1335 | 38·8 |
| 1 | 0·1064 | 77 | 0·0996 | 42 | 0·1074 | 87 | 0·1056 | 37 | 0·1146 | 63·1 |
| 2 | 0·1030 | 89 | 0·1037 | 64 | 0·1019 | 96 | 0·1100 | 59 | 0·1280 | 78·8 |
| 3 | 0·1022 | 94 | 0·1011 | 77 | 0·0997 | 100 | 0·1078 | 71 | 0·1291 | 84·7 |

*Quantitative Reduction of the ω-Bromoxylenes by Hydrogen Iodide at 25°.*

A solution of hydrogen iodide in glacial acetic acid was used which contained 0·70 gm. of HI per c.c. Approximately 0·5 gm. of the bromoxylene was dissolved in sufficient glacial acetic acid to make the volume 1 c.c. in a 5-c.c. ground glass-stoppered measuring cylinder. The reducing agent (4 c.c.) was then added and the cylinder immersed in the thermostat. The rate at which the reduction took place was determined as in a previous communication (Lapworth and Shoesmith, *loc. cit.*). The results are summarised in Table II, where *t*, *w*, and *x* have the same significance as before.

*Identification of the Reduction Products.*—Approximately 6 grams of the ω-bromoxylene and 45 c.c. of the reducing agent were used. The mixture was maintained at 25° for 40 hours and then poured into water. The solids which separated in the experiments with the ortho- and para-isomerides and also with benzyl bromide were filtered off, dried, and recrystallised from light petroleum. They

* For convenience, the results for ω-iodo-*p*-xylene (for preparation, see p. 2282) are included.

TABLE II.

| | Ortho-compound. $w=0{\cdot}5862$ gm. | Meta-compound. $w=0{\cdot}5537$ gm. | |
|---|---|---|---|
| $t$. | $x$. | $x$. | |
| ½ | — | 17·9 | The para-isomeride did not reduce under these conditions, and iodine corresponding to 2 per cent. reduction was liberated from benzyl bromide. |
| 1½ | 2·5 | 25·6 | |
| 3½ | 4·2 | 36·5 | |
| 7 | 8·2 | 50·8 | |
| 20 | 12·1 | 83·9 | |

proved to be the corresponding iodo-derivatives; ω-iodo-*o*-xylene, m. p. 33—34°, ω-iodo-*p*-xylene, m. p. 46—47° (compare Pavlovsky, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 214), and benzyl iodide, m. p. 24°. Estimations of the hydrolysable iodine confirmed this.

In addition to the solid which was obtained from the reduction product of the ortho-compound a small drop of oil was observed, but it was not possible to identify it owing to the very small quantity which separated out.

*m*-Xylene was isolated from the reduced meta-isomeride in the following way. The reduction mixture was poured into excess of water, decolorised by the addition of sodium thiosulphate, and the acid neutralised with sodium hydroxide. The whole was extracted with ether and from the ethereal extract an oil (1·5 gm.) was obtained which distilled between 135—150°. When redistilled, it boiled at 135—143°. It was identified by its density (0·857 at 16°) and its trinitro-derivative, m. p. 181—182°, which did not depress the melting point of an authentic specimen of trinitro-*m*-xylene.

*Reduction of the Iodotoluenes at 25°.*

The iodotoluenes were prepared from the toluidines. The ortho-isomeride distilled at 205° and the para at 211° (m. p. 35°).

In order to obtain the meta-isomeride perfectly free from ortho-compound, *m*-nitrotoluene was purified by means of ethyl oxalate and sodium methoxide as described by Reissert (*Ber.*, 1897, **30**, 1047). The pure *m*-nitrotoluene (m. p. 16°, b. p. 231°) was reduced with iron filings and a small quantity of acetic acid (see also Shoesmith, Hetherington, and Slater, *loc. cit.*). The toluidine, which distilled at 203°, was converted into *m*-iodotoluene, b. p. 213°, in the usual way. The explosions which took place during the last preparation, especially when it was carried out on a moderately large scale, are noteworthy, and small-scale experiments (10 gms. of *m*-toluidine) are to be recommended.

The iodotoluenes were reduced under the same conditions as were the ω-bromoxylenes, and in Table III, $t$ is the time in days

from the commencement of the experiment, whilst $w$ and $x$ have the same significance as before.

TABLE III.

| | Ortho-compound. $w = 1{\cdot}2150$ gm. | Meta-compound. 1·1934 gm. | Para-compound. 1·2051 gm. | | Ortho-compound. | Meta-compound. | Para-compound. |
|---|---|---|---|---|---|---|---|
| $t$. | $x$. | $x$. | $x$. | $t$. | $x$. | $x$. | $x$. |
| 1 | 48·4 | 4·1 | 32·1 | 6 | 88·1 | 13·3 | 79·2 |
| 2 | 67·9 | 7·9 | 50·5 | 8 | 92·0 | 17·4 | 85·9 |
| 4 | 82·8 | 10·9 | 69·9 | | | | |

From the *o*- and *p*- isomerides toluene was isolated by the method employed for the separation of *m*-xylene. It distilled at 105—118°, had density 0·876 at 16°, was quite free from halogen, and its trinitro-derivative (m. p. 81—82°) did not depress the melting point of an authentic specimen of trinitrotoluene.

Under the above conditions iodobenzene liberated iodine in a quantity which represented 10% reduction in 8 days.

The authors desire to acknowledge a grant from the Earl of Moray Research Fund which has defrayed the expenses of this investigation.

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## CCCVI.—*The Solvent Action of Trialkyl Trimethylenetriamines on Uric Acid.*

By JOHN GRAYMORE.

THE success of a number of cyclic diamines, *e.g.*, piperazine, in the treatment of rheumatism, postulated as due to their forming soluble urates, led the author to believe that the investigation of cyclic triamines of the type $(CH_2{\cdot}NR)_3$ in this connexion would not be without interest. Accordingly trimethyl- and triethyl-trimethylenetriamine were prepared, and their salts with uric acid examined. Both have a strong solvent action on uric acid *in vitro*, the urate of the former having a solubility in water of 1 part in 11 and that of the latter being soluble to the extent of 1 in 9.

The triethyl compound was submitted to a physiological examination; when given hypodermically, the solution produced all the signs of intense irritation and there were indications of toxic symptoms as well.

Both compounds formed crystalline additive products

$(CH_2{\cdot}NR)_3Br_2$, with bromine; the hydrochloride of the triethyl compound was also prepared and examined.

*Trimethyltrimethylenetriamine*, $(CH_2{\cdot}NMe)_3$, is most conveniently prepared by Henry's method. A solution of methylamine hydrochloride (33 gms.) in water (50 c.c.) was cooled in ice and, after ½ hour, gradually poured into cooled 40% formaldehyde (38 gms.; 1 mol.). After 2 hours, the hydrochloric acid was neutralised with caustic soda, the solution dehydrated over-night with caustic soda, and the supernatant yellow oil distilled, when trimethyltrimethylenetriamine passed over at 160—164°. It was redistilled several times until no odour of formaldehyde was perceptible.

*Trimethyltrimethylenetriamine urate* was prepared by heating the base and uric acid (equal mols.) in aqueous solution on the water-bath for 2 hours. The solution was then concentrated and was left to dry off in a warm place. The glassy urate, which could not be crystallised, was precipitated from alcohol as a gelatinous mass, and dried. On heating, it decomposed without melting. 0·514 gave 0·169 $N_2$; N = 32·00. $(CH_2{\cdot}NMe)_3,C_5H_4O_3N_4$ requires N = 32·99%. The solubility was determined by evaporating weighed portions of a solution, saturated at 18°, to half their bulk on a water-bath at 40° and finally dehydrating over caustic potash.

*Trimethyltrimethylenetriamine Dibromide*, $(CH_2{\cdot}NMe)_3Br_2$.—The orange-red precipitate obtained on adding strong aqueous bromine to well-cooled aqueous trimethyltrimethylenetriamine was dried and recrystallised from chloroform by the addition of a drop of light petroleum, separating in light yellow needles, m. p. 97°. 0·35 gave 0·454 AgBr; Br = 55·2. $C_6H_{15}N_3Br_2$ requires Br = 55·36%.

*Triethyltrimethylenetriamine* was prepared, after the method of Einhorn and Prettner, by the interaction of cold aqueous ethylamine and 40% formaldehyde (equal mols.) at 0°. The mixture was left for 2 hours and dehydrated over-night with caustic soda, until a portion of the alkali added remained undissolved. The base, on distillation, yielded triethyltrimethylenetriamine, b. p. 190—196°.

The *urate*, prepared in a manner similar to that of the trimethyl compound, was obtained as a pearly white, amorphous solid, which decomposed on heating without melting. 0·629 gave 0·183 $N_2$; N = 29·08. $(CH_2{\cdot}NEt)_3,C_5H_4O_3N_4$ requires N = 28·91%. Its solubility was determined as in the case of the previous base.

The *hydrochloride*, $(CH_2{\cdot}NEt)_3,HCl$, was obtained from dry hydrogen chloride and the base in a little dry ether. The bulky, white precipitate was redissolved in excess of ether and the solution evaporated in a vacuum, long, needle-like crystals being obtained. 2·51 gave 1·73 AgCl; Cl = 17·05. $C_9H_{21}N_3,HCl$ requires Cl = 17·09%.

The *dibromide*, obtained as a viscous, red oil by adding an excess of concentrated bromine water to a strong aqueous solution of the base, crystallised after 2 days to a mass of long, needle-like crystals. It was dissolved in chloroform and a drop of light petroleum added, when long, almost colourless needles, m. p. 144—145°, separated. 0·32 gave 0·363 AgBr; Br = 48·27. $C_9H_{21}N_3Br_2$ requires Br = 48·33%.

In conclusion, the author wishes to express his indebtedness to Professor F. S. Kipping, F.R.S., for his interest and advice during this investigation, and also to Dr. H. H. Dale, of the National Institute for Medical Research, for kindly undertaking a physiological examination of the products of this research.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, July 21st*, 1924.]

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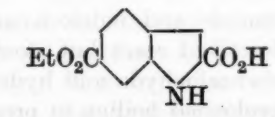
## CCCVII.—*Syntheses in the Indole Series. Part I.*

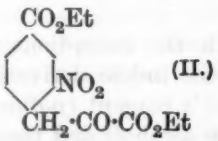
By WILLIAM OGILVY KERMACK.

IT is well known that indolecarboxylic acid and its derivatives, when condensed with an aminoacetal and treated with alcoholic hydrogen chloride, yield compounds which are either of the indolediazine or of the carboline type (Kermack, Perkin, and Robinson, J., 1921, **119**, 1602; 1922, **121**, 1872; Blaikie and Perkin, this vol., p. 296). Although at first it appeared that the effect of, for example, the insertion of a methoxyl group in the benzenoid nucleus in favouring the formation of one or of the other of these two types might be predicted from considerations of polarity, further investigation has shown that a complete explanation of the effects of such a substitution has not yet been realised (Blaikie and Perkin, *loc. cit.*).

It was considered of interest to study the effect of a positive substituent in the benzene ring. With this end in view, an attempt was made to prepare 6-carbethoxyindole-2-carboxylic acid (I)

(I.)



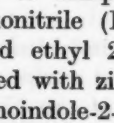



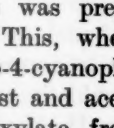

(II.)

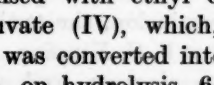
by condensing ethyl 2-nitro-*p*-toluate with ethyl oxalate in presence of sodium ethoxide, and reducing the product so obtained. However, the product of the condensation, instead of being 2-nitro-4-carbethoxyphenylpyruvic acid, as analogy with similar combin-

ations suggested would be the case, was ethyl 2-nitro-4-carbethoxy-phenylpyruvate (II). On reduction, ethyl indole-2 : 6-dicarboxylate was obtained, and on hydrolysis this yielded indole-2 : 6-dicarboxylic acid, which, of course, was not suitable for the purpose in view.

In the hope that this difficulty might be circumvented, a similar series of compounds was prepared, commencing with 2-nitro-*p*-toluonitrile (III). This, when condensed with ethyl oxalate, yielded ethyl 2-nitro-4-cyanophenylpyruvate (IV), which, when reduced with zinc dust and acetic acid, was converted into ethyl 6-cyanoindole-2-carboxylate, from which, on hydrolysis, 6-cyanoindole-2-carboxylic acid (V) was obtained. This compound was condensed with some difficulty, owing to its relative insolubility

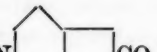
(III.) 

(IV.) 

(V.) 

in acetyl chloride, with aminodimethylacetal, and 6-cyanoindole-2-carboxydimethylacetalylamide (VI) resulted. From this compound, however, on treatment with alcoholic hydrogen chloride,

(VI.)

(VII.) 

no crystalline material could be obtained; apparently the presence of the positive cyano-group lowers the reactivity of the hydrogen atoms in the pyrrole nucleus and ring formation does not take place.

6-Cyanoindole-2-carboxylic acid readily loses carbon dioxide on heating with quicklime, with the production of 6-cyanoindole (VII), a compound which, in its general properties and colour reactions resembles indole itself. Prolonged hydrolysis with boiling methyl-alcoholic potash converts 6-cyanoindole into indole-6-carboxylic acid.

With the exceptions of 6-cyanoindole and indole-6-carboxylic acid, the indole derivatives here described react but slowly with Ehrlich's reagent (*p*-dimethylaminobenzaldehyde and hydrochloric acid in alcohol) and then only on prolonged boiling in presence of additional concentrated hydrochloric acid. This lack of reactivity is of interest in view of the failure of 6-cyanoindole-2-carboxydimethylacetalylamide to yield either a diazine or a carboline derivative.

## Experimental.

*2-Nitro-p-toluic Acid.*—*p*-Toluic acid * (27·2 gms.) is dissolved in warm nitric acid (80 c.c. of acid, *d* 1·5, and 80 c.c. of acid, *d* 1·42) and the nitrotoluic acid crystallises on cooling; water is added, and the product, m. p. 187—188°, collected (yield 32—33 gms.) (compare Fittig and Ramsay, *Annalen*, 1873, **168**, 251).

*Ethyl 2-Nitro-p-toluate.*—A solution of 2-nitro-*p*-toluic acid (40 gms.) in absolute alcohol (40 c.c.) is saturated with dry hydrogen chloride and, after 12 hours, poured into water. The ester, which is extracted with ether, is a slightly yellow oil, b. p. 163—170°/10 mm. (yield 78%; some unchanged acid is recovered).

*Ethyl 2-Nitro-4-carbethoxyphenylpyruvate* (Formula II).—A mixture of ethyl 2-nitro-*p*-toluate (20·9 gms.) and absolute alcohol (30 c.c.) is added all at once to a cold solution of sodium ethoxide (sodium 4·6 gms., absolute alcohol 70 c.c.) containing ethyl oxalate (29·2 gms.); a deep red colour develops almost at once. The mixture is kept over-night at 37°, water (50 c.c.) added (this dissolves the bright red crystals which will have separated) and then hydrochloric acid (50 c.c. of approx. 14%), slowly and with shaking, when the deep red colour disappears and a light yellow, crystalline material separates. More water is added and, after some time, the solid is collected, dried in a vacuum, and recrystallised from dilute acetic acid and then from benzene, long, silky, felted, faintly yellow needles, m. p. 88—89°, being obtained (Found: C = 54·7; H = 5·0. $C_{14}H_{15}O_7N$ requires C = 54·4; H = 4·9%). The use of sodium ethoxide in presence of ether to effect the above condensation did not prove satisfactory.

Attempts to prepare 2-nitro-4-carbethoxyphenylpyruvic acid by partial hydrolysis of the preceding ester with sodium carbonate or very dilute sodium hydroxide solution were not successful. A rather bright red solution formed, the colour of which increased on heating and then diminished, and hydrolysis of the compound took place with great ease.

*Ethyl Indole-2 : 6-dicarboxylate.*—As derivatives of ethyl *o*-nitrophenylpyruvate are not readily soluble in ammonia without decomposition, reduction by means of ammoniacal ferrous sulphate, which is so satisfactory in the preparation of indole-2-carboxylic acid from *o*-nitrophenylpyruvic acid and of the corresponding methoxy-derivatives, is not available.

Ethyl 2-nitro-4-carbethoxyphenylpyruvate (15 gms.) is dissolved in boiling acetic acid (160 c.c.), zinc dust (50 gms.) added slowly,

* I have to thank the British Dyestuffs Corporation for the *p*-toluic acid used in this investigation.

and boiling continued for about 15 minutes. The solution is filtered hot, and the undissolved zinc dust washed well with hot dilute acetic acid. On cooling, and if necessary diluting, ethyl indole-2 : 6-dicarboxylate separates in a voluminous mass of light yellow, crystalline needles. After drying in a vacuum and recrystallisation from benzene, the compound forms light yellow needles, m. p. 132° (Found : C = 64·6; H = 5·9. $C_{14}H_{15}O_4N$ requires C = 64·3; H = 5·8%). It gives no colour with alkalis.

*Indole*-2 : 6-*dicarboxylic Acid.*—The ester (1·4 gms.) is heated with 10% alcoholic potash (20 c.c.) until complete solution takes place, and there is no precipitation on dilution with water. The hot brownish-red solution, which has an intense violet fluorescence, is acidified with hydrochloric acid, and the indole-2 : 6-dicarboxylic acid, which separates as a brownish-white powder, is dried, and recrystallised from glacial acetic acid with the aid of charcoal, forming compact, white needles, which scarcely darken even at 310°. The crystals, after drying for some time at 100° and then in a vacuum, have a composition agreeing approximately with $C_{10}H_7O_4N,\frac{1}{2}C_2H_4O_2$ (Found : in material dried at 120—130°, C = 58·4; H = 3·6. $C_{10}H_7O_4N$ requires C = 58·5; H = 3·4%). With Ehrlich's reagent to which additional hydrochloric acid has been added, this acid and its diethyl ester give slowly and on prolonged boiling a slight red colour which is intensified by the addition of dilute sodium nitrite.

2-*Nitro*-p-*toluonitrile* (Formula III).—A solution of *p*-toluonitrile (20 gms.) in fuming nitric acid (100 c.c.; 94%) is, after 1 hour, diluted with water (200 c.c.). The white precipitate is recrystallised from methylated spirit, and long, stout, pale yellow needles, m. p. 107—108°, are obtained (yield 85%).

*Ethyl* 2-*Nitro*-4-*cyanophenylpyruvate* (Formula IV).—If 2-nitro-*p*-toluonitrile is added in hot alcoholic solution to a solution of sodium ethoxide and ethyl oxalate, blue compounds are formed owing to the positive cyano-group causing simultaneous oxidation and reduction as in the case of dinitrotoluene. Since, however, 2-nitro-*p*-toluonitrile is soluble in a warm mixture of ethyl alcohol and ethyl oxalate, the condensation may be carried out as follows: 2-Nitro-*p*-toluonitrile (8 gms.) is dissolved in a mixture of ethyl alcohol (30 c.c.) and ethyl oxalate (30 gms.) at about 40°, and to the solution, cooled as far as possible without separation of the nitrile, a cooled sodium ethoxide solution (sodium 2·3 gms., alcohol 100 c.c.) is added all at once. A blue coloration, lasting for only a fraction of a second, is sometimes seen, and the solution quickly becomes red. The mixture is kept over-night at 40°, the bright red deposit is dissolved by the addition of water (150 c.c.), and, on

acidifying, a voluminous, light yellow precipitate is obtained, which is collected and dried in a desiccator. On adding more water, further crops of less pure material are obtained. After two recrystallisations from benzene–light petroleum and then from alcohol, pale yellow, needle-like crystals are obtained, m. p. 107° (Found: C = 55·2; H = 3·9. $C_{12}H_{10}O_5N_2$ requires C = 55·0; H = 3·8%). Ethyl 2-nitro-4-cyanophenylpyruvate dissolves in alkalis with a red colour.

*Ethyl 6-Cyanoindole-2-carboxylate.*—Ethyl 2-nitro-4-cyanophenylpyruvate (10 gms. of the crude precipitated material) was reduced with acetic acid (200 c.c. of 50%) and zinc dust (25 gms.) in the same way as ethyl 2-nitro-4-carbethoxyphenylpyruvate (p. 2287) and gave about 6 gms. (yield 44%, calculated from the original 2-nitro-*p*-toluonitrile) of *ethyl 6-cyanoindole-2-carboxylate*, which crystallised from benzene in pale greenish-yellow needles, m. p. 171° (Found: C = 67·2; H = 4·8. $C_{12}H_{10}O_2N_2$ requires C = 67·3; H = 4·7%).

*6-Cyanoindole-2-carboxylic Acid* (Formula V).—Ethyl 6-cyanoindole-2-carboxylate (3 gms.) is warmed gently with alcoholic potash (20 c.c. of 10%) until solution is complete, water is added, and the whole heated until, on further dilution, no cloudiness is observed. The hot solution is acidified, and, after cooling, the precipitated acid is collected, washed, dried (yield 95%), and recrystallised from acetic acid, forming small needles, m. p. 290—295° (decomp.) after sintering at about 280° (Found: C = 64·6; H = 3·6. $C_{10}H_6O_2N_2$ requires C = 64·5; H = 3·3%). 6-Cyanoindole-2-carboxylic acid, and, less readily, its ethyl ester give with Ehrlich's reagent a red colour when subjected to prolonged boiling in presence of excess of hydrochloric acid. The colour is somewhat intensified by the addition of sodium nitrite.

*6-Cyanoindole-2-carboxydimethylacetalylamide* (Formula VI).—The chloride of 6-cyanoindole-2-carboxylic acid was prepared by the acetyl chloride–phosphorus pentachloride method (Kermack, Perkin, and Robinson, *loc. cit.*). To very finely divided 6-cyanoindole-2-carboxylic acid mixed with acetyl chloride (20 parts), the theoretical amount of phosphorus pentachloride is added. Owing to the insolubility of the acid, solution takes place only slowly and some difficulty is caused by the fact that the acid chloride crystallises out very readily. After warming slightly so as to complete the reaction as far as possible, the acetyl chloride is distilled off under reduced pressure, and the residue dissolved in warm chloroform and filtered. Aminodimethylacetal (2 mols.) in chloroform solution is added, and, after mixing, the solvent is evaporated under reduced pressure. On adding water, filtering, and recrystallising from ethyl alcohol, *6-cyanoindole-2-carboxy-*

*dimethylacetalylamide* is obtained in yellow needles, m. p. 215° (Found: C = 61·8; H = 5·6. $C_{14}H_{15}O_3N_3$ requires C = 61·5; H = 5·5%). When treated with Ehrlich's reagent, this compound gives no colour reaction, but when extra hydrochloric acid is added and boiling is prolonged, a red colour slowly develops, which shows green dichroism in thin layers. This colour disappears on cooling and reappears on heating. On addition of sodium nitrite the colour becomes green, and blue on heating, remaining blue on dilution with water.

6-Cyanoindole-2-carboxydimethylacetalylamide was treated with alcoholic hydrogen chloride to ascertain whether closure of the ring took place. No crystalline compound, however, could be obtained, only a somewhat viscous mass, and no fluorescence was visible. It is possible that the acetal is converted into the free aldehyde, but that the presence of the cyano-group inhibits ring formation. This decreased reactivity of the 1- and 3-hydrogen atoms, resulting from the presence of the cyano-group, is further evidenced by the increased stability of 6-cyanoindole, as compared with indole, to acids (compare below).

6-*Cyanoindole* (Formula VII).—6-Cyanoindole-2-carboxylic acid decomposes when heated, but there is much charring and none of the 6-cyanoindole can be isolated. The latter compound, however, is produced by dry distillation of an intimate mixture of the acid (1 gm.) with about an equal bulk of quicklime. The distillate, which solidifies, is dissolved in hot alcohol, mixed with water containing a little sodium carbonate, and decolorised with charcoal; on filtering and allowing to cool, flat needles of cyanoindole are obtained, m. p. 129—130°. For analysis, these are conveniently recrystallised from benzene–light petroleum (Found: C = 76·2; H = 4·3. $C_9H_6N_2$ requires C = 76·0; H = 4·3%). 6-Cyanoindole forms lustrous, flat needles, the flatness of which becomes accentuated—the crystals being practically plates—on crystallisation from water; a similar phenomenon is observed in the crystallisation of indole itself. With Ehrlich's reagent, a red colour develops in the cold, but more quickly on heating; the solution exhibits slight dichroism and has a blue tinge in thin layers which disappears on cooling. With sodium nitrite, the red colour deepens and the solution remains red on dilution. With vanillin and hydrochloric acid, a bright red colour quickly appears, which shows a trace of yellow when viewed in thin layers. On dilution, a brown precipitate forms, and with excess of caustic soda the whole becomes pale bluish-red. The pine-shaving reaction gives a rather pale violet colour. 6-Cyanoindole appears to be much more stable to acids than indole itself.

*Indole-6-carboxylic Acid.*—6-Cyanoindole is boiled with methyl-alcoholic potash under reflux for 24 hours, ammonia being gradually evolved. The alcoholic solution is diluted with water, a little charcoal added, and the filtered mixture is acidified, when indole-6-carboxylic acid separates as a white powder. When recrystallised from acetic acid, it forms white needles, m. p. 243—244° (Found: C = 67·2; H = 4·4. $C_9H_7O_2N$ requires C = 67·1; H = 4·3%). Indole-6-carboxylic acid gives with Ehrlich's reagent in the cold a red colour which becomes intense on heating. Sodium nitrite intensifies this colour, which assumes a blue tinge when viewed in thin layers.

The author is indebted to the Royal Society for a grant which defrayed part of the expenses of this research.

RESEARCH LABORATORY OF THE ROYAL COLLEGE OF PHYSICIANS, EDINBURGH. [*Received, July 22nd,* 1924.]

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# CCCVIII.—*Organic Derivatives of Silicon. Part XXX. Complex Silicohydrocarbons* $[SiPh_2]_n$.

By FREDERIC STANLEY KIPPING.

THE unsaturated silicohydrocarbon (A) and the saturated compound (B), which are obtained by the action of sodium on diphenylsilicon dichloride (Kipping and Sands, J., 1921, **119**, 830), have the molecular formula $Si_4Ph_8$,* and it has been shown that the structure of the former is best represented by ...$SiPh_2$·$SiPh_2$·$SiPh_2$·$SiPh_2$..., whereas the latter is doubtless an octaphenyl*cyclo*silicotetrane (Kipping, J., 1923, **123**, 2590).

Two more of the reaction products which accompany (A) and (B) have now been examined, namely, those provisionally denoted by (C) and (D) respectively (Kipping and Sands, *loc. cit.*, p. 836). The results point to the conclusion that the relationship between these two substances is similar to that between (B) and (A).

The compound (C) is a very well-defined silicohydrocarbon, $[SiPh_2]_n$. Although no difficulty was experienced in proving its composition, its molecular weight could not be determined, owing

* Although there was no reason to doubt the accuracy of the cryoscopic results previously obtained with (B) (J., 1921, **119**, 846), some further experiments have been made. Found: in benzene, $M = 750, 736$; in camphor, $M = 739$ as the mean of six concordant observations. $Si_4Ph_8$ requires $M = 729·6$. To check the camphor method, determinations were made with tetra-anhydrotetrakisdiphenylsilicanediol. Found: $M = 759$ as a result of six concordant values. Calculated for $Si_4Ph_8O_4$, $M = 793·6$.

to its very slight solubility in all organic media. It is, moreover, a very unreactive substance and it has been impossible to obtain any evidence of its molecular formula by converting it into other compounds.

In its stability towards iodine, boiling tetrachloroethane, and boiling nitrobenzene, (C) differs entirely from the unsaturated compound (A) and resembles octaphenyl*cyclo*silicotetrane (B). Further, (C) is not attacked to an appreciable extent by alkalis or by piperidine; here again it differs entirely from (A) and resembles (B), which is only very slowly decomposed by these reagents.

On this evidence, (C) might be regarded with some assurance as a dodecaphenyl*cyclo*silicohexane, $[SiPh_2]_6$, formed from 1 mol. of $SiPh_2Cl{\cdot}SiPh_2Cl$ and 1 mol. of $SiPh_2Cl{\cdot}[SiPh_2]_2{\cdot}SiPh_2Cl$, or as a hexadecaphenyl*cyclo*silico-octane formed from 2 mols. of the latter: the fact that (C), compared with (B), is so very sparingly soluble in organic solvents points to the more complex formula.

The substance (D) has not been obtained in definite crystals, but only in the form of a nearly colourless, slightly gelatinous powder. For practical purposes, it is insoluble in all organic solvents which were tried, and could only be purified by extracting from it all soluble matter. The results of silicon determinations, confirmed to some extent by those of combustions (compare p. 2295), pointed to the formula $[SiPh_2]_n$, which, of course, is rendered highly probable by the method of formation of the substance; this formula was fully established by the results of determinations of the hydrogen value of (D) (Kipping and Sands, J., 1921, **119**, 848). Towards certain reagents (D) appears to be stable; thus, like (B) and (C), it is not appreciably attacked by boiling tetrachloroethane or by iodine, in which respects it differs entirely from (A). On the other hand, like (A), it is very readily decomposed by alkalis and piperidine, and is completely converted into diphenylsilicanediol and a mixture of its condensation products, with evolution of hydrogen, $>SiPh_2 + 2H_2O = SiPh_2(OH)_2 + H_2$; further, (D) is readily oxidised by nitric acid and by permanganate, and is decomposed by boiling nitrobenzene.

The evidence on which to base a constitutional formula for (D) is scanty and somewhat contradictory, although there seems to be no doubt that the substance is highly complex and that its molecule consists entirely of $>SiPh_2$ groups. In spite of the fact that it does not behave like an unsaturated compound towards iodine, its insolubility, the readiness with which it is oxidised, and especially its behaviour towards alkalis, point strongly to a much closer relationship with (A) than with (B) or (C). It is therefore suggested that the molecule of (D), like that of (A), contains two tervalent

silicon atoms, and may be represented by ... $SiPh_2 \cdot [SiPh_2]_4 \cdot SiPh_2$ ... or perhaps more probably ... $SiPh_2 \cdot [SiPh_2]_6 \cdot SiPh_2$ ... The inertness of (D) towards iodine and certain other halogenated reagents which attack (A) might then be attributed to a more pronounced masking of the two tervalent silicon atoms than that which has been assumed to exist in the case of (A) (Kipping, J., 1923, **123**, 2599); in the latter compound, the tervalent silicon atoms can be combined with halogens and with ethyl groups, but apparently not with phenyl groups; it is therefore conceivable that if 2 mols. of (A) were united to form the more complex structure assigned to (D), the phenyl groups combined with the two tervalent silicon atoms might be pushed so closely together as to inhibit the introduction of an iodine atom.

The main product of the action of sodium on diphenylsilicon dichloride is still under investigation.

## EXPERIMENTAL.

*The Silicohydrocarbon* (C).—The compound (C) is deposited together with (A), from the toluene extract (Kipping and Sands, *loc. cit.*, p. 836), but unless the extraction has been very prolonged a considerable proportion of (C) remains in the blue mineral residue: this remainder is obtained together with (D) when the blue salt is treated, first with a mixture of alcohol and acetic acid and then with water. The separation of (C) from (D) can be accomplished by a prolonged extraction of the mixture with boiling benzene or toluene, but the complete separation of (C) from (A) by fractional crystallisation is much more troublesome. The most rapid and satisfactory method for the preparation of pure (C) is to suspend the mixture in benzene, add iodine in excess, and finally filter the solution of the di-iodide $Si_4Ph_8I_2$ from the undissolved (C): the washed residue is then dissolved in and crystallised from benzene. It may be stated without hesitation that such preparations are pure (Found: C = 78·7, 78·8; H = 5·8, 5·9; Si = 15·1, 15·2, 15·4. $SiPh_2$ requires C = 79·0; H = 5·4; Si = 15·6%).

The compound leaves a colourless residue when it is burnt in oxygen, and also when it is cautiously ignited with a mixture of nitric and sulphuric acids, so the above results are trustworthy; a very violent reaction takes place when (C) is treated with the acid mixture and unless great care is taken the percentage of silicon found is low.

When heated in a test tube, (C) does not melt even at very high temperatures; it chars slightly and gives vapours which take fire with a distinct explosion. The crystals of (C) obtained from benzene solution at the ordinary temperature are very small, but

exceptionally well-defined; under the microscope they are seen to consist of highly lustrous, transparent, six-sided pyramids and rhombohedra. These crystals become opaque and white owing to the loss of solvent when they are exposed to the air during a few minutes, so it is easy to detect the presence of (C) in samples of (A) and *vice versâ*. Crystals from toluene are only poorly defined and apparently do not contain solvent. For comparison with that of (A), the solubility of (C) was roughly determined; 100 gms. of benzene at about 75° dissolve approximately 0·6 gm., most of which is deposited as the solution cools to 15°; the solubility in boiling toluene is about 0·7. In other ordinary solvents, including melted camphor, (C) is not appreciably soluble, but it dissolves in boiling benzyl alcohol rather more readily than in benzene and separates again in flat, well-defined, six-sided prisms. (C), unlike (A), seems to be quite unchanged when it is boiled with tetrachloroethane or with nitrobenzene; it is only very sparingly soluble in these solvents and separates from the former in microscopic, rhomboidal crystals. It does not react with iodine even in boiling toluene solution and it also seems to be unchanged by bromine in chloroform solution at the ordinary temperature. When it is warmed during many hours with acetic acid containing nitric acid, no change seems to occur, nor is it altered when it is boiled with 50% nitric acid.

Attempts to obtain the hydrogen value of (C) failed; it is not acted on by alcoholic sodium hydroxide solution, or by a heated mixture of piperidine and sodium hydroxide containing some water; a portion which had been heated during 3 hours at about 220° with sodium ethoxide was recovered unchanged and not a trace of diphenylsilicol seemed to have been formed.

*The Silicohydrocarbon* (D).—For the isolation of (D), the dark blue residue of sodium and sodium chloride in which it is contained (Kipping and Sands, *loc. cit.*, p. 836) was added, in small portions at a time, to a mixture of alcohol and acetic acid, but even when the acid was kept in excess, it is possible that a local and temporary alkalinity of the solution caused some decomposition. When all the sodium had dissolved, water was added, the somewhat greyish, flocculent solid exhaustively washed with boiling water, dried, and then extracted continuously with boiling benzene for 16 hours, until it appeared to be free from (C); the extractions with boiling water and with boiling benzene were then repeated, each occupying many hours.

Many different preparations of the grey, somewhat gelatinous product thus obtained and dried at 110°, gave silicon percentages agreeing satisfactorily with those required for a silicohydrocarbon $[SiPh_2]_n$ (Found: Si = 15·2, 15·7, 15·4. Calc., Si = 15·6%), but

the hydrogen values varied from about 100 to 114 (theor. 123). Such preparations, in addition to filter-paper fibres, still contained traces of (C), but not enough to account for the low hydrogen values; it seemed, therefore, that some oxidation of (D) occurred during the prolonged extractions which were necessary to remove the mineral matter and (C), both of which were very tenaciously retained. As direct experiments confirmed this inference (see below), the method of purification was modified; the blue sodium chloride was first extracted with boiling toluene until apparently free from (C), then treated with alcohol and acetic acid as described above, and the insoluble matter washed with water by a process of diffusion extending over some weeks; the product was then washed with acetone and extracted several times with large volumes of hot benzene, all these operations being carried out without the use of filter-paper.

Such preparations dried in a vacuum gave hydrogen values of 122·8 and 124·3, and therefore consisted of pure silicohydrocarbon, $[SiPh_2]_n$. Attempts to determine the carbon percentage were by no means successful, as the residue of silica generally retained carbon even at the highest temperatures which could be used; the best result obtained was C = 78·5, H = 5·5; calculated for $[SiPh_2]$, C = 79·0, H = 5·5%. The estimation of the carbon in the silica residues with the aid of hydrofluoric acid was of little use, because the whole of the silica which was formed did not remain in the boat.

When quickly heated on platinum foil, (D) does not melt, but puffs, leaving a residue which cannot, as a rule, be obtained free from carbon, even on prolonged ignition; the compound decomposes violently when it is covered with sulphuric acid and then treated with a few drops of nitric acid, but the residue of silica which is finally obtained on ignition is usually quite free from carbon.

No organic liquid of the many which were tried dissolves any appreciable quantity of (D) as such, but when the compound is boiled during many hours with water, it gives a faintly yellow solution and is converted to a slight extent into substances soluble in acetone and benzene: it would seem, therefore, that (D), like (A), undergoes atmospheric oxidation, or that the action of water is analogous to that of alkalis. In spite of its insolubility, (D) is much more readily oxidised by an acetic acid solution of nitric acid than (A), (B), or (C); when heat is applied, a vigorous action sets in and the compound is quickly and completely converted into soluble products. The latter, with the exception of a minute proportion of an unrecognised crystalline compound, seem to consist entirely of an oily mixture of the condensation products of diphenylsilicanediol, since they gradually dissolve in alcoholic potassium hydroxide

solution without the evolution of hydrogen; after expelling the alcohol completely, the clear liquid gives a precipitate of diphenylsilicanediol on the addition of an acid. (D) is also oxidised by an acetic acid solution of potassium permanganate, but here again only the condensation products of diphenylsilicanediol seem to be formed.

When (D) is warmed with nitrobenzene, it swells up and gives a gelatinous product, but no appreciable chemical change seems to occur if the liquid is heated at its boiling point during some minutes; at the end of some hours, however, the solution has become dark in colour and ultimately practically the whole of (D) has disappeared. The product is a dark brown oil, which on hydrolysis with alcoholic potassium hydroxide solution gives no hydrogen, and except for a little carbonaceous matter seems to be entirely transformed into the potassium derivative of diphenylsilicanediol.

When (D) is treated with a benzene solution of iodine there seems to be no action even at about 75°; when, after it has been heated during several hours, the solution is filtered, the filtrate contains nothing but iodine and the washed residue consists apparently of the unchanged silicohydrocarbon, somewhat coloured by adsorbed halogen.

A warm alcoholic solution of potassium hydroxide attacks (D) with unexpected readiness; hydrogen is rapidly evolved and after a short time the whole of the insoluble substance has disappeared; the clear solution, when freed from alcohol, still remains clear and gives a heavy precipitate of diphenylsilicanediol on the addition of an acid. The compound is decomposed by a mixture of piperidine and aqueous alkali even at the ordinary temperature, and at 80—90° a steady evolution of hydrogen occurs until decomposition is complete; the hydrogen value is therefore easily and accurately determined. On the addition of water to the piperidine–alkali solutions, a crystalline or oily precipitate is obtained according to the conditions maintained; from one solution tetra-anhydrotetrakis-diphenylsilicanediol was directly isolated, but in all cases the whole of the products could be converted into a substance (diphenylsilicanediol) soluble in aqueous alkalis and precipitated in needles on the addition of an acid. If the sample of (D) had been incompletely freed from (C), the crystals of the latter could be detected in the piperidine–alkali solution at the end of the reaction.

From the qualitative and quantitative results obtained in the determination of the hydrogen value of (D), it must be concluded that the compound is a silicohydrocarbon $[SiPh_2]_n$ and that its molecule does not contain either a $-SiPh_3$ or a $>SiPh-$ group (compare J., 1923, **123**, 2598).

The author desires to express his thanks to the Grant Committee of the Royal Society for a grant which enabled him to purchase from Boots Pure Drug Co. a supply of diphenylsilicon dichloride for the purpose of this research.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 20th,* 1924.]

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## CCCIX.—*The Isomerism of the Oximes. Part XX. The Isomeric* p-*Nitrobenzophenoneoximes and their Four Methyl Ethers.*

By O. L. BRADY and R. P. MEHTA.

THE Hantzsch-Werner stereochemical hypothesis of the isomerism of the oximes demands the existence of four isomeric ethers, an oxygen and a nitrogen ether corresponding to each of the two isomeric oximes.

$$\begin{array}{llll} \mathrm{R{\cdot}C{\cdot}R'} & \mathrm{R{\cdot}C{\cdot}R'} & \mathrm{R{\cdot}C{\cdot}R'} & \mathrm{R{\cdot}C{\cdot}R'} \\ \mathrm{AlkO{\cdot}N} & \mathrm{N{\cdot}OAlk} & \mathrm{O{:}NAlk} & \mathrm{AlkN{:}O} \end{array} \text{ or } \left[\begin{array}{l} \mathrm{R{\cdot}C{\cdot}R'} \\ \mathrm{O{<}NAlk} \end{array}\right] \text{ or } \left[\begin{array}{l} \mathrm{R{\cdot}C{\cdot}R'} \\ \mathrm{AlkN{>}O} \end{array}\right]$$

Although two isomeric *O*-ethers had been obtained from certain aldoximes and ketoximes (the position is summarised by Brady and Dunn, this vol., p. 294), until 1918 all attempts to obtain a second *N*-ether had been unsuccessful; the second *N*-benzyl ether of furfuraldoxime described by Hantzsch and Werner (*Ber.*, 1890, **23**, 2336, 2764) was shown to be a hydrate by Goldschmidt and Zanoli (*Ber.*, 1892, **25**, 2573), whilst one of the two supposed *N*-methyl ethers of benzaldoxime (Luxmore, J., 1896, **69**, 183) and of *p*-methoxybenzaldoxime (Goldschmidt, *Ber.*, 1890, **23**, 2186; Beckmann and Netscher, *Annalen*, 1909, **356**, 201) was also proved to be a hydrate (Scheiber, *Annalen*, 1909, **356**, 215). Semper and Lichtenstadt (*Ber.*, 1918, **51**, 928), however, obtained two *N*-methyl ethers of *p*-tolylketoxime, but although they isolated also two *O*-methyl ethers, one was an uncrystallisable oil and therefore of uncertain purity. In view of the importance of these compounds as a strong support of a stereochemical as against a purely structural explanation of the isomerism of the oximes and of the criticisms of Atack (J., 1921, **119**, 1175), it seemed desirable that an oxime should be studied from which all four ethers could be obtained in a crystalline state; *p*-nitrobenzophenoneoxime was chosen, since experience had shown that *p*-nitro-substituted oximes usually give well-crystallised and high-melting derivatives.

Subsequent to the commencement of this work, Plowman and

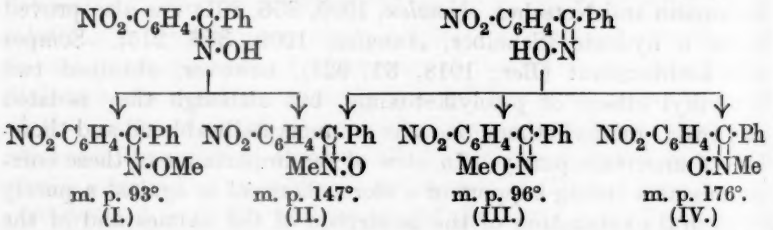
Whiteley (this vol., p. 587) have described four crystalline isomeric methyl ethers from the oximes of mesoxmono-*p*-tolylamide,

$$H_2N\cdot CO\cdot C(:NOH)\cdot CO\cdot NH\cdot C_7H_7,$$

two *O*-ethers and two *N*-ethers. Certain complications are, however, introduced in this case in view of the existence of five forms of the parent oxime, and critics of the stereochemical theory might argue that the presence of the carbonyl groups and consequent opportunities of tautomerism introduce some ambiguity.

Oximation of *p*-nitrobenzophenone gave a mixture of the isomeric oximes and great difficulty was experienced in isolating the individuals, fractional crystallisation from various solvents proving useless. Separation was ultimately achieved by taking advantage of the sparing solubility of the sodium salt of one isomeride in cold 2*N*-sodium hydroxide. The configuration of the two isomerides was determined by the Beckmann change. *anti-p*-Nitrobenzophenoneoxime gave *p*-nitrobenzanilide, and *syn-p*-nitrobenzophenoneoxime a mixture of benzo-*p*-nitroanilide and *p*-nitrobenzanilide, the former predominating; the *syn*-isomeride, being the labile form, behaving as is usual in giving a mixture of the two anilides (Hantzsch, *Ber.*, 1891, **24**, 13). In order to avoid confusion, the usual convention of a *cis*-interchange of radicals has been adopted in assigning the prefixes *syn-* and *anti-* to the oximes (compare, however, Meisenheimer and co-workers, *Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289).

On methylation, *anti-p*-nitrobenzophenoneoxime gave *anti-p*-nitrobenzophenoneoxime *O*-methyl ether (I) and *anti-p*-nitrobenzophenoneoxime *N*-methyl ether (II), whilst *syn-p*-nitrobenzophenoneoxime gave *syn-p*-nitrobenzophenoneoxime *O*-methyl ether (III), *syn-p*-nitrobenzophenoneoxime *N*-methyl ether (IV) together with some *anti-p*-nitrobenzophenoneoxime *N*-methyl ether (II).




The constitution of the ethers was determined by warming with hydriodic acid; the two *O*-ethers gave quantitative yields of methyl iodide and the two *N*-ethers gave no methyl iodide, but methylamine was detected in the solution.

$$RR'C{:}N\cdot OMe + H_2O \longrightarrow RR'CO + \underset{\text{α-methylhydroxylamine}}{H_2N\cdot OMe} \xrightarrow{HI} NH_3 + CH_3I + H_2O$$

$$RR'C{:}N(Me){:}O + H_2O \longrightarrow \underset{\beta\text{-methylhydroxylamine}}{RR'CO + NHMe{\cdot}OH} \xrightarrow{HI} NH_2Me + H_2O.$$

The two *O*-ethers differed in crystalline form as seen under the microscope and, although their melting points were close together, a mixture of equal parts of each melted at 67—76°; the two *N*-ethers also differed in crystalline form and a mixture of equal parts melted at a lower temperature than either separately (125—135°). The molecular weights were normal in all four cases. There seems no doubt, therefore, of the entity of the four compounds.

The two *O*-ethers of *p*-nitrobenzophenoneoxime are not readily interconvertible by means of hydrogen chloride, although the *syn-O*-methyl ethers of the aldoximes isomerise into their *anti*-derivatives under these conditions. The stability of these ethers militates against the suggestion of Atack (J., 1921, **119**, 1182) that the second *O*-ether might have the structure $>C\!-\!\overset{\uparrow\uparrow}{N}$ . OR

The formation of a mixture of approximately equal amounts of the two *N*-ethers from *syn-p*-nitrobenzophenoneoxime demands some consideration. One of the *N*-ethers from the oxime of mesoxmono-*p*-tolylamide described by Plowman and Whiteley (*loc. cit.*) is readily converted into the other isomeride by acids and solvents, but the *N*-methyl ethers from the *p*-nitrobenzophenoneoximes, once formed, do not seem to be readily interconvertible, since they can be crystallised unchanged from hot solvents. Acids, however, decompose them easily, giving the ketone. If the production of the *N*-ether of *anti-p*-nitrobenzophenoneoxime were due to the presence of *anti*-oxime in the *syn*-oxime employed, or to change of *syn*- into *anti*-oxime during the reaction, one would expect that the two *O*-ethers would also be formed in about equal quantities; this, however, was not the case, no evidence of the formation of the *anti-O*-ether being obtained. It appears, therefore, that the isomerisation must occur at the moment of formation of the *N*-ether from the oxime, probably through the rearrangement of an intermediate additive compound (compare Brady, J., 1914, **105**, 2104).

We have adopted the nitrone structure, $R_2C{:}N(R){:}O$, for the *N*-ethers. Some reasons for this have been given previously (Brady, *loc. cit.*). Recently, Auwers and Ottens (*Ber.*, 1924, **57**, [B], 446) have favoured this structure from a study of the optical characters of the ethers of the oximes, but the most important evidence is that of Staudinger, Miescher, and Schlenker (*Helv. Chim. Acta*, 1919, **2**, 554).

The action of acetic anhydride on both *anti*- and *syn-p*-nitrobenzophenoneoximes gave the acetyl derivative of the *anti*-oxime,

as indicated by hydrolysis. In the case of a number of other unsymmetrical ketoximes both acetyl derivatives have been obtained, although the acetyl compound from the labile oxime passed very easily into that from the stable oxime (Hantzsch, *Ber.*, 1890, **23**, 2776; Demuth and Dittrich, *ibid.*, 3609; Schafer, *Annalen*, 1891, **264**, 158; Hantzsch, *Ber.*, 1891, **24**, 54; Smith, *ibid.*, 4031); our failure is probably due to the instability of acetyl-*syn*-*p*-nitrobenzophenoneoxime.

Phenylcarbimide gave with both oximes the carbanilino-derivative of the *anti*-oxime. Hantzsch (*Ber.*, 1890, **23**, 2776) obtained carbanilino-*anti*-*p*-tolylphenoneoxime from both *p*-tolylphenoneoximes, but states that the carbanilino-derivatives of the *p*-bromobenzophenoneoximes are more stable, referring to the work of Auwers and Meyer (*Ber.*, 1890, **23**, 2063); there is, however, no mention of two isomeric carbanilino-derivatives in this paper, nor can we find any reference in the literature to the isolation of two isomeric carbanilino-derivatives of an unsymmetrical ketoxime.

## Experimental.

In the preparations here described, careful attention must be paid to details; the separations are difficult and the methods given were found to be the best after many trials with numerous solvents.

*Oximation of* p-*Nitrobenzophenone*.—The ketone (70 g.), prepared by Schroeter's method (*Ber.*, 1909, **42**, 3360), was suspended in alcohol (700 c.c.), a concentrated aqueous solution of hydroxylamine hydrochloride (75 g.) added slowly, the mixture kept overnight and then heated for 3 hours on the water-bath under reflux, when a clear, brown solution was obtained; after cooling, removing the *p*-nitrobenzophenone which separated, diluting with water (2½ l.), the solution was kept on ice until the precipitated oil solidified. After washing and drying in an evacuated desiccator, a mixture of the two isomeric oximes was obtained, m. p. 95—108°. About 1 per cent. of the ketone was unattacked.

anti-p-*Nitrobenzophenoneoxime* (formula corresponding to I).—The above mixture was dissolved in the minimum amount of 2*N*-sodium hydroxide at 80—90°, the clear solution cooled, and after 30 minutes the precipitated golden-yellow leaflets of the sodium salt of the *anti*-oxime were collected, washed with a little cold 2*N*-sodium hydroxide, redissolved in hot 2*N*-sodium hydroxide, and the hot filtered solution was saturated with carbon dioxide. The precipitate (m. p. 138—148°), after washing and crystallising three times from alcohol, gave pure anti-p-*nitrobenzophenoneoxime*, $C_{13}H_{10}O_3N_2$, very pale yellow, prismatic crystals, m. p. 158° [0·2703 gave 27·8 c.c. $N_2$ at 22·8° and 744 mm. N = 11·7 (11·6)]. The

compound decomposed slowly on keeping, but was more stable when preserved in the dark over solid sodium hydroxide in a vacuum.

syn-p-*Nitrobenzophenoneoxime* (formula corresponding to III.).—The mother-liquor separated from the sodium salt above was saturated with carbon dioxide, and the rather pasty precipitate (m. p. 94—107°) washed, dried in a desiccator, and dissolved in the minimum amount of hot alcohol; on cooling, a small quantity of a product (m. p. 118—124°) separated and was collected. The solution was then cooled, first in ice and then in a freezing mixture, and a series of fractions obtained, m. p.'s 112—116°, 108—112° and finally 102—107°. Partial dilution with water gave a product, m. p. 95—104°, and further dilution an oil together with a small amount of solid, m. p. 112—116°; the oil was rejected. The first product (m. p. 118—124°), on dissolving in the minimum amount of hot alcohol and cooling to 0°, gave a solid, m. p. 129—135° (impure *anti*-oxime), and the filtrate at — 20° a product, m. p. 113—118°. After a long series of crystallisations, in which, at first, the *anti*-oxime was eliminated in the least soluble portion, syn-p-*nitrobenzophenoneoxime*, $C_{13}H_{10}O_3N_2$, was obtained as a buff-coloured, micro-crystalline powder, m. p. 115°, decomposing, on keeping, more rapidly than the *anti*-isomeride [0·2704 gave 27·6 c.c. $N_2$ at 22·5° and 744 mm. N = 11·5 (11·6)].

*Determination of Configuration.*—An ice-cooled, dry, ethereal solution of the oxime (1 g.) was treated with finely powdered phosphorus pentachloride (1·5 g.); after a short time the solvent was removed and water added. *anti-p*-Nitrobenzophenoneoxime gave a solid identified after crystallisation from alcohol as *p*-nitrobenzanilide (m. p. 214°) by comparison with another specimen and hydrolysis to aniline and *p*-nitrobenzoic acid.*

*syn-p*-Nitrobenzophenoneoxime gave a crude amide, m. p. 148—165°, which could not be separated into its components on account of the small quantity available, but hydrolysis gave a mixture of aniline and *p*-nitroaniline; the latter, which predominated, was isolated.

*Methylation of* anti-p-*Nitrobenzophenoneoxime.*—The oxime (10 g.) was dissolved in an ice-cooled solution of sodium hydroxide (4·5 g.) in water (25 c.c.) and methyl alcohol (10 c.c.), methyl sulphate (5 g.) added in small portions, the mixture left on ice for 15 minutes, and the mother-liquor poured off from the brown, viscous mass which had separated. The mother-liquor was extracted with a little ether, which was then used to wash the residue in the reaction flask; after a second wash with a very small amount of ether, a granular solid remained, m. p. 70—82°. The ether washing, on evaporation, gave

* *p*-Nitrobenzanilide is described as melting at 204°, but a specimen prepared from aniline and *p*-nitrobenzoyl chloride melted at 214°.

a small quantity of brown oil which was not further investigated. The solid was extracted with warm ether, the residue being a yellow powder, m. p. 128—138°. The ethereal solution, on dilution with an equal volume of light petroleum and keeping, gave a small amount of the same material, which was added to the main bulk, whilst the solution was kept for the isolation of the *O*-ether. The solid, after crystallising four times from methyl alcohol and once from benzene, gave 4·4 g. of the N-*methyl ether* of anti-p-*nitrobenzophenoneoxime* $C_{14}H_{12}O_3N_2$ (II) as shining, yellow plates, m. p. 147° [0·2700 gave 25·3 c.c. $N_2$ at 16·8° and 753 mm.; 0·1500 in 17·63 benzene gave depression of 0·161°. N = 11·0 (10·9); *M* = 268 (256)]. Heating with hydriodic acid gave no methyl iodide, but methylamine was identified in the reaction mixture by decolorising with sulphurous acid, adding excess of sodium hydroxide, and distilling into an alcoholic solution of 2 : 4-dinitrochlorobenzene, when 2 : 4-dinitromethylaniline was obtained.

The ether–light petroleum solution above was evaporated at room temperature and the pasty residue extracted with hot light petroleum, the extract being decanted from the small amount of oily residue. On removing the solvent and crystallising the residue six times from methyl alcohol, 4 gms. of the O-*methyl ether* of anti-p-*nitrobenzophenoneoxime*, $C_{14}H_{12}O_3N_2$ (I), was obtained as faintly yellow leaflets, m. p. 93° [0·2700 gave 25·2 c.c. $N_2$ at 16·8° and 753 mm.; 0·3500 gave 0·3238 AgI; 0·1500 in 17·59 benzene gave depression of 0·174°. N = 10·9 (10·9); OMe = 12·2 (12·1); *M* = 249 (256)].

*Methylation of* syn-p-*Nitrobenzophenoneoxime*.—On methylating the oxime as above, a solid separated which was washed and dried in an evacuated desiccator over sodium hydroxide. Ether dissolved most of it; the residue had m. p. 110—125°. The ethereal solution was diluted with light petroleum (2 vols.), kept on ice for 20 minutes, the precipitate (m. p. 108—122°) added to the above residue, and the solution kept for isolation of the *O*-ether. Repeated crystallisation of the solid from diluted methyl alcohol, acetone, or benzene failed to give a pure product, the crystals separating melting at 124—136°, whereas dissolution in the minimum amount of cold methyl alcohol, in which the solid was readily soluble, and cooling in a freezing mixture furnished a minute amount of material, m. p. 152—159°. Microscopic examination indicated that the product, m. p. 124—136°, was a mixture of a new *N*-ether and the *N*-ether from the *anti*-oxime in about equal proportions. Separation was ultimately achieved by dissolving in the minimum amount of chloroform, adding light petroleum drop by drop until a slight permanent turbidity was produced, and cooling in a freezing mixture for 15 minutes. The precipitate (m. p. 146—152°), after

crystallising 4 times from hot benzene, gave 1·8 gms. of the N-*methyl ether* of syn-p-*nitrobenzophenoneoxime*, $C_{14}H_{12}O_3N_2$ (IV), as a bright yellow, crystalline powder, m. p. 176° [0·2200 gave 20·6 c.c $N_2$ at 17·2° and 754 mm.; 0·1500 in 17·47 benzene gave depression of 0·162°. N = 11·0 (10·9); *M* = 269 (256)]. Hydriodic acid gave methylamine, identified as above.

The ether–light petroleum solution above was evaporated at the ordinary temperature, the brown, viscous oil separated from the crystalline material by cautious washing with small quantities of a mixture of ether (1 vol.) and light petroleum (2 vols.), and the residue crystallised 4 times from methyl alcohol, giving 4 gms. of the *O-methyl ether* of syn-p-*nitrobenzophenoneoxime*, $C_{14}H_{12}O_3N_2$ (III), colourless prisms, m. p. 96° [0·2703 gave 25·0 c.c. $N_2$ at 17·6° and 755 mm.; 0·3500 gave 0·3222 AgI; 0·1500 in 17·34 benzene gave depression of 0·176°. N = 10·8 (10·9); OMe = 12·2 (12·1); *M* = 249 (256)].

*Action of Hydrogen Chloride on the Isomeric Ethers and Oximes.*—A solution of each *O*-ether in dry ether was saturated with dry hydrogen chloride. No hydrochloride was precipitated and on evaporation at room temperature the original compounds were recovered, melting but 1—2° lower; absence of change was shown by the method of mixed melting points. Similarly, solutions of the *N*-ethers in benzene first became turbid and then cleared, an oil separating; from this and from the solution, *p*-nitrobenzophenone was obtained, but no *N*-ether, indicating decomposition of the latter, the necessary water being obtained from the atmosphere during manipulation. When a solution in dry ether of either of the oximes was saturated with hydrogen chloride, no hydrochloride was formed, the precipitate being the unchanged oxime, which is less soluble in ether containing hydrogen chloride than in pure ether.

*Acetyl*-anti-p-*nitrobenzophenoneoxime*, $NO_2{\cdot}C_6H_4{\cdot}\overset{\displaystyle N{\cdot}OAc}{\overset{\|}{C}}{\cdot}Ph$.—The *anti*-oxime (3 gms.), dissolved in cold acetic anhydride (5 c.c.), was poured into sodium carbonate solution, the precipitate after washing, drying in a vacuum over sodium hydroxide, and crystallising from benzene, gave the *acetyl* compound, $C_{15}H_{12}O_4N_2$, colourless needles, m. p. 178° [0·3165 gave 27·4 c.c. $N_2$ at 22·6° and 746 mm. N = 9·9 (9·9)]. After hydrolysis with 2*N*-sodium hydroxide (0·3 gm. to 20 c.c.) on the water-bath for 30 minutes and cooling to 0°, the sodium salt of the *anti*-oxime crystallised, from which the oxime was obtained and identified. The same acetyl derivative, as shown by the method of mixed melting points and by hydrolysis, was obtained from the *syn*-oxime even at — 25° with every precaution to prevent isomeric change.

*Carbanilino*-anti-p-*nitrobenzophenoneoxime*, $NO_2 \cdot C_6H_4 \cdot \underset{\underset{NO \cdot CO \cdot NHPh}{\|}}{C} \cdot Ph$ —A solution of the *anti*-oxime (2·5 gms.) in dry ether was mixed with phenylcarbimide (1·5 gms.) in a well-stoppered bottle. After 40 minutes, the precipitate (m. p. 181° decomp.) was crystallised from chloroform, when the carbanilino-compound was obtained as a white, crystalline powder, m. p. 181° decomp. [0·2500 gave 25·2 c.c. $N_2$ at 21·5° and 739 mm. N = 11·4 (11·6)].

On hydrolysis (0·5 gm. in 40 c.c. of 2*N*-NaOH) for 2 hours, the compound dissolved and, on cooling, the sodium salt of the *anti*-oxime crystallised, from which the *anti*-oxime was obtained and identified. The *syn*-oxime, on treatment in a similar manner, gave a crude product sintering at 152° and melting and decomposing at 165—175°. This was found to be somewhat impure carbanilino-*anti*-*p*-nitrobenzophenoneoxime by comparison with the previous compound and by hydrolysis to the *anti*-oxime. The rather low melting point of the crude product seems to indicate that there was some carbanilino-*syn*-*p*-nitrobenzophenoneoxime present, but the amount was too small to be isolated.

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## CCCX.—*Resolution of α-Terpineol.*

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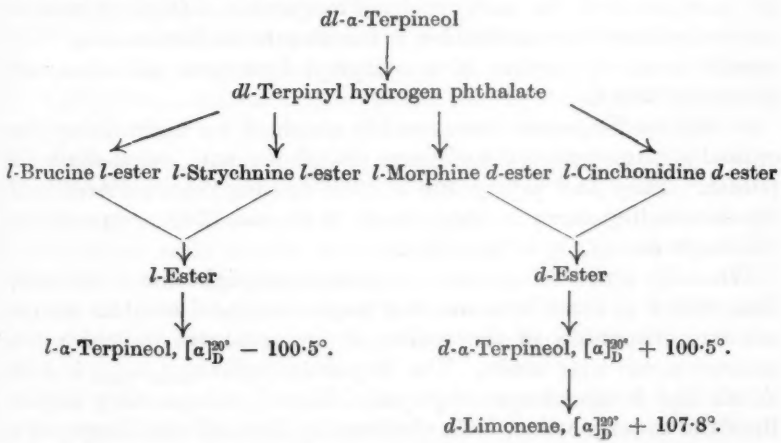
THE methods which have been employed for the preparation of optically active α-terpineol are of two distinct types, (i) those starting with an optically active substance, either natural or synthetic, which by various chemical reactions can be converted into optically active terpineol, (ii) those starting with optically inactive terpineol, which either as the compound itself, or in the form of one of its derivatives, is caused to combine with an optically active substance, the resulting mixture of stereoisomerides being separated by fractional crystallisation. The following examples of the first method may be mentioned. By the action of alcoholic sulphuric acid on *l*-pinene Flawitzky (*Ber.*, 1879, **12**, 2354) obtained *l*-α-terpineol, a result which was confirmed by Godlewsky (*Chem. Zentr.*, 1899, 1241). By the hydrolysis of limonene hydrochloride with aqueous potassium hydroxide Wallach (*Annalen*, 1906, **350**, 154) prepared an optically active terpineol, and later (*ibid.*, 1908, **360**, 98), by the action of dilute sulphuric acid on methylnopinol (pinene hydrate), he obtained α-terpineol with a high lævorotation

the constants of which agree very closely with those of the *l*-terpineol described in this communication. Stephen (*J. pr. Chem.*, 1898, [ii], **58**, 109), by the action of acetic anhydride on *l*-linalool, obtained a mixture of geraniol and *d*-α-terpineol. W. H. Perkin (J., 1908, **93**, 1871), by the interaction of magnesium methyl iodide and the *d*- and *l*-forms of ethyl 1-methyl-$\Delta^1$-*cyclo*hexene-4-carboxylate, synthesised optically active α-terpineols. These terpineols, however, were not optically pure, since their rotatory powers are considerably below the highest recorded values for naturally occurring α-terpineol. The only example of the second method of preparing active terpineol is that due to Windaus (*Z. physiol. Chem.*, 1923, **126**, 308), who found that terpineol forms compounds with digitonin of which the less soluble in aqueous alcohol was that of *l*-α-terpineol. In this way, he obtained less than a gram of α-terpineol which had $[\alpha]_D - 101°$ in ethereal solution.

The present communication describes the resolution of α-terpineol by a method which has been used by one of us for the resolution of secondary alcohols, but which, up to the present, has failed in the case of tertiary alcohols containing the hydroxyl group attached to the asymmetric carbon atom.

The fractional crystallisations of the brucine and of the morphine salts of α-terpinyl hydrogen phthalate gave pure *l*-brucine *l*-terpinyl phthalate and *l*-morphine *d*-terpinyl phthalate respectively. Decomposition of these salts with dilute acid yielded the pure acid esters ($[\alpha]_D \pm 36{\cdot}7°$, $c = 5$ in ethyl-alcoholic solution),* which, on hydrolysis, gave pure *d*- and *l*-α-terpineols, $[\alpha]_D^{20°} \pm 100{\cdot}5°$. The results are indicated by the following diagram




* The authors' polarimetric observations of solutions were all made at this concentration.

The brucine salt of α-terpinyl hydrogen phthalate, readily prepared from the ester in methyl-alcoholic or acetone solution, gave, on systematic crystallisation, the pure *l*B, *l*A salt. Similarly, the strychnine salt, submitted to a similar process in ethyl-alcoholic solution, gave the corresponding pure *l*B, *l*A salt. The rate of resolution of this salt was slower than that of the corresponding brucine salt, but there are the considerable practical advantages of its lesser solubility and its more compact crystalline character. The partly dextrorotatory terpinyl hydrogen phthalate recovered from the mother-liquors of the brucine and strychnine salts was converted into the morphine salt, which, when systematically recrystallised from methyl alcohol, gave the pure *l*B, *d*A salt. A portion of the *d*-hydrogen phthalic ester obtained by the decomposition of the pure morphine salt was converted into the very soluble cinchonidine salt, which slowly crystallised from acetone in fine, silky needles. This salt, on decomposition, yielded α-terpinyl hydrogen phthalate of unchanged rotatory power. Samples of terpinyl hydrogen phthalate were thus obtained possessing rotatory powers of equal magnitude by the crystallisation of four different alkaloidal salts, in all cases until constancy of rotatory power had been reached. The possibility of mixed crystals occurring in every one of these four salts at the same point must be very remote.

The preparation of pure *d*-terpinyl hydrogen phthalate by the recrystallisation of the partly resolved product from acetic acid or benzene is not nearly so effective as by the crystallisation of the alkaloidal salts (compare Kenyon, J., 1922, **121**, 2540). Similarly, the purification of the partly resolved magnesium α-terpinyl phthalate by fractional crystallisation is too slow to be serviceable. The specific rotatory powers of *d*-α-terpinyl hydrogen phthalate are given in Table I.

d- *and* l-α-*Terpineols* were readily obtained by hydrolysing the optically pure terpinyl hydrogen phthalates with ethyl-alcoholic potash. They had $[\alpha]_D^{20^\circ} \pm 100{\cdot}5^\circ$; the melting points, determined by the cooling-curve method, were 36·9° and 37·0°, respectively (Wallach, *loc. cit.*, gives 37—38°).

When $1/\alpha$ is plotted against $\lambda^2$, a perfectly straight line is obtained, from which it must be concluded that α-terpineol exhibits simple rotatory dispersion in the region of the spectrum in which the measurements were made. The dispersion ratio $\alpha_{4358}/\alpha_{5461}$ is 1·73 at all the temperatures employed. This is considerably higher than the average value, 1·63, obtained by Pickard and Kenyon for aliphatic alcohols.

The rotatory dispersion of α-terpineol appears also to be simple

when the rotatory powers are determined in 4—5% solution in the following solvents—ethyl alcohol, benzene, *cyclo*hexane, chloroform, carbon disulphide, ether.

Solution in chloroform, ethyl alcohol, ether, or *cyclo*hexane has but little effect on the rotatory power of terpineol; benzene causes slight exaltation, whilst carbon disulphide brings about increase in specific rotatory power to the extent of 30%. The temperature coefficient of rotation of terpineol in the homogeneous state is very small; the observed rotations show a maximum at about 60° and the specific rotatory powers at 90°. The curves obtained when $[\alpha]_\lambda$ is plotted against temperature are, for each wave-length, smooth curves slightly concave to the temperature axis.

An attempt was also made to effect the resolution of α-terpineol by the fractional crystallisation of the hydrogen *d*-camphorate of *dl*-terpineol. This compound, which is readily prepared by the interaction of the potassium derivative of terpineol and *d*-camphoric anhydride in benzene solution, crystallises well from acetic acid in fine, hard rhombs which melt at 127—128°, but recrystallisation from this solvent or from benzene altered the rotatory power of the substance at a very slow rate. The ester combines with *d*-α-phenylethylamine to form a salt which melts at 115—117°, but this was not resolved on fractional crystallisation from acetone.

Fractional precipitation of potassium *dl*-terpinyl *d*-camphorate with an aqueous solution of brucine hydrochloride gave only a very slow resolution, nor was fractional crystallisation from acetone of the cinchonidine, cinchonine, brucine, or strychnine salt any more successful.

d-*Limonene*.—There appears to have been a tendency for investigators to class as dipentene (or limonene) any dehydration product of α-terpineol. Dipentene, however, is a somewhat unstable compound and readily undergoes isomeric change to terpinolene or the terpinenes, particularly in presence of acid reagents; *inter alios*, Wallach (*Annalen*, 1893, **275**, 104) states that heating α-terpineol with oxalic acid gives almost pure terpinolene. The very small differences in density and refractive index of these compounds make the task of differentiation somewhat difficult. The chief point of difference between them is that whilst limonene is optically active, terpinolene and the terpinenes possess no asymmetric carbon atom and are optically inactive.

Since limonene is so unstable to acid reagents, the dehydration of terpineol was effected by an alkaline reagent, use being made of the observation that, when terpinyl hydrogen phthalate is hydrolysed by means of *aqueous* potassium hydroxide, a considerable amount

of dehydration accompanies the hydrolysis. A solution of *d*-terpinyl hydrogen phthalate in an excess of aqueous sodium hydroxide solution was distilled with steam. From the volatile products, two fractions were very easily separated, the one of lower boiling point mobile and smelling strongly of lemons, the other of higher boiling point viscous and setting completely to a crystalline mass on cooling. Approximately 2 parts of *d*-α-terpineol to 1 part of *d*-limonene were obtained. The rotatory power, $[\alpha]_D^{20°} + 107{\cdot}8°$, of the limonene was unaltered by redistillation. Wallach and Conrady (*Annalen*, 1889, **252**, 145) give $[\alpha]_D^{8°} + 106{\cdot}8°$ ($c = 14{\cdot}4$) in chloroform solution; and Wallach (*ibid.*, 1888, **246**, 222) gives $[\alpha]_D - 105°$ ($c = 6{\cdot}1$) in ethyl-alcoholic solution.

It would thus appear that the close agreement between the rotatory powers of the *l*-α-terpineol obtained by the method described in this communication and of the *l*-α-terpineol obtained by Wallach from pinene hydrate, together with the additional close agreement between the rotatory powers of the *d*-limonene obtained as described above by the dehydration of *d*-α-terpineol and of the *d*-limonene prepared by Wallach and Conrady, may be taken as furnishing further evidence in support of the view that the terpineols and the limonene described herein are substances in the optically pure condition.

Since terpineol is a tertiary alcohol which readily suffers loss of water, the ordinary methods for the preparation of the optically active *n*-aliphatic esters had to be considerably modified.

*d*-α-Terpinyl formate was prepared in quantitative yield by the interaction at the ordinary temperature of *d*-terpineol and the mixed anhydride of formic and acetic acids (Béhal, *Ann. chim. phys.*, 1900, [vii], **20**, 411). The corresponding acetate, propionate, *n*-butyrate, and *n*-valerate were prepared from *l*-terpineol by first converting it into the compound $C_{10}H_{17}{\cdot}O{\cdot}MgCl$ by the action of magnesium ethyl chloride in ethereal solution and subsequently adding the calculated amount of the requisite acid anhydride in ethereal solution (Houben, *Ber.*, 1898, **31**, 1736). In all four cases, the yields of ester were good—the only detectable impurity being a small amount of unesterified terpineol which was easily removed by careful redistillation. The esters are colourless, mobile liquids; the formate, acetate, and propionate possess sweet, terpene-like odours, whereas the butyrate and valerate have fainter, but not unpleasant, odours more characteristic of the acid part of the molecule. They possess rotatory powers, both in the homogeneous state and in solution, of the same sign as that of the terpineol from which they are derived. For these five esters, when $1/\alpha$ is plotted against $\lambda^2$, straight lines, within the limits of experimental error,

are obtained, except possibly in the case of the propionate. The effects of the different solvents on the rotatory powers of each of the esters are qualitatively the same.

The values of the various physical constants which are tabulated in the experimental part show, in general, a smooth progression as the length of the ester chain increases. When the specific rotatory powers of the esters in the homogeneous state are plotted against molecular weight, the otherwise smooth curve shows a slight irregularity at the propionate; this irregularity is increased when the rotatory powers are determined in solution. The specific rotatory powers of the esters of α-terpineol therefore conform to the type usually met with in homologous series of esters of this kind derived from secondary alcohols (J., 1923, **123**, 1). There is, however, one interesting difference, namely, that the specific rotatory power of the alcohol itself lies on the same smooth curve as those of the esters derived from it.

## Experimental.

*α-Terpinyl Hydrogen Phthalate.*—The principal products of the reaction between α-terpineol and phthalic anhydride at 100—110° are unsaturated hydrocarbons, as is indeed the case with most tertiary alcohols (compare Pickard, Lewcock, and Yates, P., 1913, **29**, 106). Terpinyl hydrogen phthalate can be obtained much more consistently by a slight modification of Tiemann and Kruger's method (*Ber.*, 1896, **29**, 901) for the preparation of linalyl hydrogen phthalate. The clear solution produced by the interaction of finely powdered potassium * (39 gms.) and terpineol (165 gms.) in warm benzene (2½ litres) is added slowly to a solution of phthalic anhydride (148 gms.) in benzene (1½ litres), when a considerable evolution of heat takes place. After 12 hours, the thick reaction mixture is added cautiously to crushed ice and water (with precaution against ignition of the benzene), the benzene solution extracted three times with dilute sodium carbonate, and the united aqueous layer and extracts are acidified, when *terpinyl hydrogen phthalate* is precipitated as an oil which quickly sets to a hard, crystalline mass. It separates from acetic acid (2 parts) in stout, prismatic rods, m. p. 117—118° (yield of pure product nearly 80%). 1·070 required 35·55 c.c. of 0·0997 *N*-sodium hydroxide; $M = 302$ (calc. 302). Dissolved in carbon tetrachloride, the hydrogen phthalate decolor-

* Sodium reacts very sluggishly with terpineol. There is a considerable difference between sodium and potassium in their reactivity towards tertiary alcohols, *e.g.*, whilst sodium has practically no action on methylethyl-*n*-propylcarbinol at its boiling point (140°), potassium reacts quite vigorously at the ordinary temperature.

ises the theoretical amount of bromine for one double bond. Recrystallisation ten times from acetic acid of the α-terpinyl hydrogen phthalate thus prepared did not alter the melting point, so that it appears to be a perfectly homogeneous compound.

*Brucine Salt of α-Terpinyl Hydrogen Phthalate.*—Crystallisation of this salt from methyl alcohol is a more satisfactory method of resolution than crystallisation from acetone, the disadvantage of the great solubility of the salt even in cold methyl alcohol being far more than counterbalanced by the regular separation which it effects. From each of these solvents the brucine salt separates in rhombic crystals, m. p. 150°. The course of the resolution may be briefly outlined. A solution of 2000 gms. of the brucine salt in 1500 c.c. of hot methyl alcohol was allowed to crystallise. The first crop of crystals was removed, and a second crop obtained by concentrating the filtrate. The second filtrate, on decomposition, yielded 155 gms. of terpinyl hydrogen phthalate with $[\alpha]_D + 16{\cdot}0°$. The first main crop was recrystallised with the following results: after two crystallisations, the $[\alpha]_D$ of the terpinyl hydrogen phthalate was $-13°$, after five $-25{\cdot}5°$, after nine $-32°$, after thirteen $-34°$, after fifteen $-35{\cdot}6°$, after seventeen $-36{\cdot}7°$. The last value was unchanged after six more crystallisations.

By systematic working up of the various mother-liquors, other crops were obtained which were recrystallised until constancy of rotation was reached. In all cases the terpinyl hydrogen phthalate had $[\alpha]_D - 36{\cdot}7°$ ($\pm 0{\cdot}1°$).

A portion of this terpinyl hydrogen phthalate was converted into the strychnine salt, which was recrystallised five times from ethyl alcohol, separating in prismatic needles, m. p. 207°. The hydrogen phthalic ester recovered from this salt was of unchanged rotatory power.

Some of the terpinyl hydrogen phthalate ($[\alpha]_D + 16°$) recovered from the mother-liquors of the brucine salt was combined with morphine, and the salt (440 gms.) crystallised from methyl alcohol (300 c.c.). It formed stout, ill-defined, rhombic crystals, m. p. 142°. The course of the resolution is shown by the following results: $[\alpha]_D$ of terpinyl hydrogen phthalate after five crystallisations was $+31{\cdot}8°$, after nine $+34{\cdot}9°$, after sixteen $+36{\cdot}4°$, after nineteen $+36{\cdot}6°$, after twenty-five $+36{\cdot}7°$.

Other crops, obtained by the systematic working up of the mother-liquors, were recrystallised until constancy of rotation was reached. In no case, however, was a sample of terpinyl hydrogen phthalate obtained with a rotatory power greater than $+36{\cdot}7°$.

*Hydrolysis of* d- *and* l-*α-Terpinyl Hydrogen Phthalates.*—Hydro-

lysis with *alcoholic* potassium hydroxide (2½ mols.) on the water-bath proceeded smoothly but slowly and no trace was developed of the odour of limonene which is produced when *aqueous* potash is employed as hydrolysing agent. After 4 hours, hydrolysis having proceeded to the extent of about 50%, the alcohol was removed, and the residue poured into water and extracted with ether. The terpineol distilled constantly at 104°/15 mm. and crystallised at once on cooling (compare Perkin, *loc. cit.*). The residual aqueous layer from which the terpineol had been extracted was acidified, and the precipitated hydrogen phthalic ester recovered from it was again submitted to hydrolysis with alcoholic potassium hydroxide. The terpineol obtained by this second treatment possessed the same rotatory power as that obtained from the first hydrolysis. The hydrogen phthalate (about one-eighth of the original quantity) remaining after a second repetition of the process was unaltered in rotatory power. The quantities obtained of *l*-α-terpineol and *d*-α-terpineol with $[\alpha]_D^{20^\circ} \pm 100{\cdot}5^\circ$ in the homogeneous state were in the ratio 14 : 12.

The *phenylurethane* of the pure *d*-α-terpineol, when crystallised from light petroleum and then from methyl alcohol, was obtained in long, prismatic needles, m. p. 109·5° (the *dl*-compound has m. p. 113°; Wallach, *Annalen*, 1893, **275**, 104). The *nitrosochloride* of *d*-α-terpineol, prepared by Perkin's method, crystallises from aqueous methyl alcohol in lustrous leaflets, m. p. 107—108°, a value identical with that obtained by Wallach (*ibid.*, 1908, **360**, 90) for the nitrosochloride of the *l*-terpineol which he prepared from methylnopinol, whereas the *dl*-compound melts at 120—122° (Wallach, *ibid.*, 1893, **277**, 121). The specific rotatory powers are very large ($[\alpha]_{4358} + 555^\circ$), possibly on account of the system of conjugated double bonds present in the molecule. If its somewhat complicated molecular structure is considered, it is rather surprising that this compound in solution exhibits simple rotatory dispersion.

TABLE I.

*Specific Rotatory Power of* d-α-*Terpinyl Hydrogen Phthalate in Various Solvents at the Ordinary Temperature.*

Length of observation tube 20 cm.

| Solvent. | Gms. of substance in 100 c.c. of solution. | Observed rotation. λ 6708. | λ 5893. | λ 5461. | λ 4358. | $[\alpha]_\lambda$. λ 6708. | λ 5893. | λ 5461. | λ 4358. |
|---|---|---|---|---|---|---|---|---|---|
| Ethyl alcohol ..... | 5·21 | +2·89° | +3·83° | +4·48° | +7·30° | +27·8° | +36·7° | +43·0° | +70·1° |
| Chloroform ..... | 5·40 | 3·34 | 4·55 | 5·14 | 8·55 | 30·9 | 41·2 | 47·6 | 79·1 |
| Carbon disulphide ... | 2·61 | 1·78 | 2·42 | 2·85 | 4·74 | 34·1 | 46·4 | 54·6 | 90·8 |
| Carbon disulphide ... | 4·74 | 2·49 | 3·26 | 3·81 | 6·25 | 25·2 | 34·4 | 40·2 | 65·9 |

## TABLE II.

*Specific Rotatory Power of* d-α-*Terpineol in the Homogeneous State at Various Temperatures.*

| $t°$. | $d_{4°}^{t°}$. | λ 6708. | λ 5896. | λ 5780. | λ 5461. | λ 4358. |
|---|---|---|---|---|---|---|
| 20° | 0·940 | +74·5° | +100·5° | +104·7° | +119·2° | +206·0° |
| 40 | 0·9235 | 76·2 | 103·6 | 108·5 | 123·0 | 213·8 |
| 60 | 0·907 | 77·6 | 105·5 | 111·0 | 125·7 | 218·6 |
| 80 | 0·890 | 79·0 | 106·6 | 111·7 | 127·2 | 220·7 |
| 100 | 0·870 | 79·0 | 106·3 | 111·2 | 126·8 | 219·5 |
| and at 21° | | 223·6 | 234·2 | 255·4 | 277·0 | 298·0 |
| for λ | | 4206 | 4126 | 3990 | 3880 | 3761 |

*Observed Densities,* $d_{4°}^{t°}$ (capacity of pyknometer about 3 c.c.).

d-α-*Terpineol,* 0·9475 at 11·5°; 0·9179 at 45·5°; 0·8945 at 74·5°; 0·8729 at 97°; 0·8525 at 120°.

l-α-*Terpineol,* 0·9402° at 19·5°; 0·9388 at 21·5°; 0·9364 at 25°; 0·9269 at 36·5°; 0·9158 at 50°; 0·9078 at 59·5°.

*Formate,* 0·9889 at 12·7°; 0·9710 at 36·0°; 0·9530 at 53·5°; 0·9400 at 72·3°.

*Acetate,* 0·9659 at 20°; 0·9384 at 51°; 0·9206 at 70°; 0·9032 at 91°.

*Propionate,* 0·9525 at 22°; 0·9350 at 40·7°; 0·9197 at 59·7°; 0·9029 at 79°.

n-*Butyrate,* 0·9455 at 18·5°; 0·9182 at 53°; 0·9064 at 68°; 0·8862 at 92°.

n-*Valerate,* 0·9424 at 16°; 0·9183 at 45°; 0·9062 at 60°; 0·8910 at 79·5°.

### d-α-*Terpineol.*

*Observed Rotatory Powers.*

Length of tube 50 mm.

| | | | | | |
|---|---|---|---|---|---|
| $t°$ | 17·5° | 43° | 67° | 90·5° | 105° |
| $\alpha_{4358}$ | 96·41 | 98·46 | 98·50 | 96·93 | 94·81 |
| $t°$ | 17·5° | 43·5° | 67° | 90·5° | 109° |
| $\alpha_{5461}$ | 55·75 | 56·95 | 56·83 | 56·04 | 54·33 |
| $t°$ | 17·5° | 43·5° | — | 90·5° | 107° |
| $\alpha_{5780}$ | 49·08 | 50·10 | — | 49·03 | 48·06 |
| $t°$ | 17·5° | 43° | 68° | 90·5° | 101° |
| $\alpha_{5896}$ | 47·02 | 48·00 | 47·56 | 46·86 | 46·13 |
| $t°$ | 17·5° | 42° | 67·5° | 90·5° | 101° |
| $\alpha_{6708}$ | 35·23 | 35·01 | 35·17 | 34·96 | 34·41 |

Photographic determinations at 21°.

Extinction at Å.U. 4355, 4206, 4126, 3990, 3880, 3765.

Polarimeter setting 96·6°, 105·0°, 110·0°, 120·0°, 130·0°, 140·0°.

*Molecular Refractivities of* α-*Terpineol and Esters, observed and calculated.*

| | $t°$. | $n_{obs.}$ | $[R_L]_D$. | Diff. from calc. | Obs. diff. for $CH_2$. |
|---|---|---|---|---|---|
| α-Terpineol ..... | 20·0° | 1·4819 | 46·73 | −0·15 | — |
| Formate ..... | 20·0 | 1·4712 | 51·77 | −0·07 | — |
| Acetate ..... | 19·7 | 1·4657 | 56·23 | −0·03 | 4·5 |
| Propionate ..... | 20·0 | 1·4641 | 60·77 | −0·05 | 4·5 |
| n-Butyrate ..... | 19·5 | 1·4632 | 65·29 | −0·09 | 4·5 |
| n-Valerate ..... | 19·5 | 1·4633 | 69·83 | −0·11 | 4·5 |

The above are calculated from the values given by Brühl. His difference for $CH_2$ is 4·56.

*Rotatory Power of* d-α-*Terpineol in Various Solvents at the Ordinary Temperature.*

Length of observation tube 20 cm.

| Solvent. | Gms. in 100 c.c. of solution. | $\alpha_\lambda$. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | $[\alpha]_\lambda$. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Carbon disulphide ..... | 5·09 | +25·56° | +14·58° | +12·79° | +12·12° | +9·10° | +251·2° | +143·3° | +125·7° | +119·2° | +89·4° |
| Ethyl alcohol ..... | 4·82 | 20·05 | 11·69 | 10·18 | 9·81 | 7·32 | 208·0 | 121·3 | 105·6 | 101·8 | 76·0 |
| Benzene ..... | 5·22 | 24·38 | 14·07 | 12·33 | 11·86 | 8·80 | 233·4 | 134·7 | 118·0 | 113·5 | 84·2 |
| Chloroform ..... | 5·15 | 21·52 | 12·43 | 10·86 | 10·52 | 7·84 | 208·8 | 120·6 | 105·4 | 102·1 | 76·1 |
| *cyclo*Hexane ..... | 4·00 | 17·10 | 10·00 | 8·74 | 8·31 | 6·24 | 213·7 | 125·0 | 109·2 | 103·9 | 78·0 |
| Ether ..... | 3·93 | 17·09 | 9·81 | 8·66 | 8·37 | 6·37 | 217·3 | 125·5 | 110·1 | 106·4 | 81·1 |
| ,, ..... | 2·00 | 8·61 | 5·08 | 4·47 | 4·22 | 3·18 | 214·8 | 126·7 | 111·5 | 105·3 | 79·3 |
| ,, ..... | 13·66 | 57·50 | 33·62 | 29·89 | 28·71 | 21·04 | 210·4 | 123·0 | 109·4 | 105·1 | 77·0 |

*Rotatory Powers of*
l-*Brucine* l-α-*Terpinyl Phthalate.*

Length of observation tube 20 cm. $t = 17°$.

| Solvent. | Gms. in 100 c.c. of solution. | Observed rotation. λ 6708. | λ 5893. | λ 5461. | λ 4358. | $[\alpha]_\lambda$. λ 6708. | λ 5893. | λ 5461. | λ 4358. |
|---|---|---|---|---|---|---|---|---|---|
| Ethyl alcohol | 2·34 | −0·50° | −0·76° | −0·98° | −2·02° | −10·7° | −16·2° | −20·9° | −43·2° |
| l-*Brucine* d-α-*Terpinyl Phthalate.* | | | | | | | | | |
| Ethyl alcohol ..... | 2·38 | +0·41° | +0·37° | +0·34° | +0·12° | + 8·6° | + 7·8° | + 7·2° | + 2·5° |
| l-*Strychnine* l-α-*Terpinyl Phthalate.* | | | | | | | | | |
| Chloroform ..... | 1·72 | — | −1·44° | −1·85° | −3·26° | — | −41·8° | −53·8° | −94·8° |

*Rotatory Power of Esters of* d-α-*Terpineol in the Homogeneous State at Room Temperature.*

Length of observation tube 25 mm. (for the formate, 50 mm.).

| | Observed rotations. | | | | | | $[\alpha]_\lambda$. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ester. | λ 4358. | λ 4916. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | λ 4358. | λ 4916. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
| Formate | +90·35° | +66·17° | +52·11° | +45·71° | +43·63° | +32·73° | +182·9° | +134·0° | +105·5° | +92·53° | +88·32° | +66·25 |
| Acetate | 36·90 | 29·14 | 23·01 | 20·22 | 19·38 | 14·54 | 163·3 | 120·2 | 94·88 | 83·38 | 79·92 | 59·95 |
| Propionate | 36·61 | — | 20·73 | 18·23 | 18·01 | 13·42 | 152·7 | — | 86·48 | 76·05 | 75·12 | 55·98 |
| *n*-Butyrate | 34·22 | 25·71 | 20·01 | 17·73 | 16·73 | 12·51 | 143·9 | 108·2 | 84·16 | 74·56 | 70·36 | 52·80 |
| *n*-Valerate | 30·80 | 23·32 | 18·42 | 16·15 | 15·46 | 11·62 | 130·0 | 98·6 | 77·89 | 68·29 | 65·20 | 49·13 |

*Photographic Determinations.*

| | Observed extinction. | | | | $[\alpha]_\lambda$. | | | |
|---|---|---|---|---|---|---|---|---|
| | λ 4375. | λ 4125. | λ 3925. | λ 3880. | λ 4375. | λ 4125. | λ 3925. | λ 3880. |
| | for α | α | α | α | | | | |
| *n*-Valerate | +30·4° | +35·4° | +40·4° | +41·4° | +128·5° | +149·7° | +170·8° | +175·1°. |

*Rotatory Powers of Esters of* d-α-*Terpineol in Ethyl-alcoholic Solution.*

Length of observation tube 20 cm. $t = 20°$.

| | | Observed rotation. | | | | | $[\alpha]_\lambda$. | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ester. | Gms. in 100 c.c. of solution. | λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
| Formate | 3·82 | +12·87° | +7·40° | +6·55° | +6·39° | +4·73° | +168·1° | +96·9° | +85·8° | +83·7° | +61·9° |
| Acetate | 3·00 | 8·70 | 5·12 | 4·50 | 4·38 | 3·23 | 144·9 | 85·3 | 74·9 | 73·0 | 53·8 |
| Propionate | 2·30 | 6·30 | 3·73 | 3·31 | 3·17 | 2·40 | 136·9 | 81·1 | 71·9 | 68·9 | 52·2 |
| *n*-Butyrate | 2·03 | 5·03 | 2·97 | 2·60 | 2·52 | 1·98 | 124·1 | 73·3 | 64·2 | 62·2 | 48·8 |
| *n*-Valerate | 2·05 | 4·84 | 2·91 | 2·59 | 2·47 | 1·88 | 118·2 | 71·0 | 63·2 | 60·3 | 45·9 |

*Rotatory Powers of Esters of* d-α-*Terpineol in Carbon Disulphide Solution.*

Length of observation tube 20 cm. $t = 20°$.

*Rotatory Powers of Esters of* d-α-*Terpineol in Carbon Disulphide Solution.*

Length of observation tube 20 cm. $t = 20°$.

| Ester. | Gms. in 100 c.c. of solution. | Observed rotation. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | $[\alpha]_\lambda$. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Formate | 3·81 | +13·27° | +7·71° | +6·80° | +6·46° | +4·94° | +174·0° | +101·1° | +89·2° | +84·7° | +64·8° |
| Acetate | 3·05 | 9·56 | 5·58 | 4·90 | 4·62 | 3·45 | 156·6 | 91·4 | 80·3 | 75·7 | 56·5 |
| Propionate | 2·47 | 7·46 | 4·41 | 3·86 | 3·65 | 2·80 | 151·2 | 89·3 | 78·2 | 73·9 | 56·7 |
| *n*-Butyrate | 2·21 | 6·06 | 3·52 | 3·06 | 3·00 | 2·28 | 137·1 | 80·6 | 69·3 | 67·9 | 51·6 |
| *n*-Valerate | 2·57 | 6·72 | 3·96 | 3·42 | 3·23 | 2·42 | 130·7 | 77·0 | 66·5 | 62·8 | 49·1 |

*Rotatory Powers of Esters of* d-α-*Terpineol in Benzene Solution.*

Length of observation tube 20 cm. $t = 20.°$

| Ester. | Gms. in 100 c.c. of solution. | Observed rotation. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | $[\alpha]_\lambda$. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Formate | 3·60 | +11·22° | +6·48° | +5·75° | +5·86° | +4·15° | +155·7° | +89·9° | +79·8° | +77·1° | +57·7° |
| Acetate | 3·14 | 8·47 | 4·89 | 4·29 | 4·15 | 3·10 | 134·6 | 77·7 | 68·2 | 66·0 | 49·3 |
| Propionate | 1·86 | 4·68 | 2·76 | 2·43 | 2·35 | 1·80 | 121·1 | 74·4 | 65·5 | 63·4 | 48·5 |
| *n*-Butyrate | 2·35 | 5·18 | 3·09 | 2·74 | 2·64 | 1·88 | 110·0 | 65·6 | 58·2 | 56·9 | 40·0 |
| *n*-Valerate | 2·50 | 5·40 | 3·24 | 2·83 | 2·78 | 2·02 | 108·1 | 64·9 | 56·7 | 55·7 | 39·8 |

*Rotatory Power of* d-α-*Terpineol Derivatives.*

Length of observation tube 20 cm. $t = 20°$.

| | Solvent. | Gms. in 100 c.c. of solution. | Observed rotations. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. | $[\alpha]_\lambda$. λ 4358. | λ 5461. | λ 5780. | λ 5893. | λ 6708. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenyl-urethane. | Chloro-form. | 1·37 | +2·19° | +1·30° | +1·17° | +1·12° | +0·87° | +80·1° | +47·5° | +42·8° | +40·9° | +31·9° |
| Nitroso-chloride. | Ethyl alcohol. | 0·87 | 9·58 | 5·38 | 4·69 | 4·45 | 3·29 | 555·2 | 310·1 | 270·3 | 256·5 | 189·6 |

*Refractive Index of α-Terpinyl Esters.*

| Ester. | $t°$. | $\lambda_{4358°}$ | $\lambda_{5461°}$ | $\lambda_{5790°}$ | $\lambda_{5896°}$ | $\lambda_{6708°}$ |
|---|---|---|---|---|---|---|
| Formate ..... | 20·0° | 1·4833 | 1·4735 | 1·4717 | 1·4712 | 1·4680 |
| Acetate ..... | 19·7 | 1·4778 | 1·4680 | 1·4663 | 1·4657 | 1·4632 |
| Propionate ..... | 20·0 | 1·4757 | 1·4664 | 1·4646 | 1·4641 | 1·4610 |
| *n*-Butyrate ..... | 19·5 | 1·4747 | 1·4654 | 1·4638 | 1·4632 | 1·4602 |
| *n*-Valerate ..... | 19·5 | 1·4750 | 1·4656 | 1·4640 | 1·4633 | 1·4603 |

The authors desire to thank the Government Grant Committee of the Royal Society for a grant with the aid of which much of the material used in this investigation was purchased. One of them was in receipt of a maintenance grant from the Department of Scientific and Industrial Research, for which he wishes to express his indebtedness.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, July 17th*, 1924.]

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## CCCXI.—*Equilibrium across a Parchment Membrane in the Case of Sodium Chloride in Presence of Sodium Caseinate.*

By PERCY ARCHIBALD SPORING.

THE inequality of the concentrations of an electrolyte on the two sides of a parchment membrane, when an electrolytic colloid is present on one side, was first noticed by Donnan and Harris (J., 1911, **99**, 1554) during measurements of the osmotic pressure of solutions of Congo-red. This "membrane equilibrium" has been investigated, both on the theoretical and the practical sides, by Donnan and others (*Z. Elektrochem.*, 1911, **17**, 572; *Proc. Roy. Soc.*, 1914, *A*, **90**, 433; J., 1914, **105**, 1941; 1919, **115**, 1313), and the physiological aspect of the subject has been studied by Sörensen (*Compt. rend. Lab. Carlsberg*, 1915, **12**, 1) and Loeb ("Proteins and the Theory of Colloidal Behaviour"). It was considered desirable to determine whether the theory verified in these researches could be applied to the case of such complicated electrolytic colloids as the salts of the proteins, and for this purpose it was decided to use an alkali salt of casein.

Casein forms two well-defined salts with alkali, neutral to litmus and to phenolphthalein, respectively (Pauli, "Colloid Chemistry of the Proteins," p. 83). The latter salt, the so-called "basic sodium caseinate," was used, because it contains the larger amount of base.

A solution of crude sodium caseinate (400 g.) in water (10 litres) was filtered from insoluble matter through several layers of muslin

and then as rapidly as possible through ordinary filter-paper, whereby most of the opacity was removed. By treatment with 10% acetic acid, the casein was flocculated at the isoelectric point, care being taken to reach this point as nearly as possible, otherwise the casein was precipitated in a form difficult to wash and dry. The precipitated casein, having been well washed with water, was treated with very dilute sodium hydroxide solution in amount just sufficient to dissolve it, the solution was filtered through muslin, and the casein reprecipitated with acetic acid. This process of solution and precipitation was repeated three times. The casein finally obtained was freed as far as possible from water, washed in a Büchner funnel with absolute alcohol, kept for 24 hours under absolute alcohol, and then extracted with alcohol and with ether, in each case for two periods of 3 hours. During these processes, if the casein, or a solution of it, had to be kept for any considerable time, it was placed in a cold store in order to prevent bacterial decomposition. The casein was finally maintained at 35° in an air-bath for 24 hours to remove the last traces of water and ether. The product was a finely divided, grey powder which gave a water-clear solution in caustic soda.

Dissolution of the light, dry powder, which is not easily wetted by water and tends to float on the surface, was effected by carefully covering it with water (100 g.) and adding $N/10$-sodium hydroxide, sufficient to dissolve the casein, but not enough to render it neutral to phenolphthalein. The mixture was diluted with water to approximately its final volume, left until the casein had completely dissolved, and then made neutral to phenolphthalein with $N/10$-sodium hydroxide.

*Apparatus and Method.*—The equilibrium vessels were similar to those used by Donnan and Allmand (*loc. cit.*), and a plain parchment membrane was employed. In agreement with Sackur and Laqueur's statement (*Beit. Chem. Physiol. Path.*, 1902, **3**, 193), it was found that the amount of sodium caseinate passing through the membrane was negligible.

Bacterial decomposition was prevented by the addition of a few drops of toluene to the solutions.

The solution of sodium caseinate (*ca.* 100 c.c.) was placed in one compartment of the distribution vessel, and in the other an equal volume of aqueous sodium chloride of known strength, the two compartments being separated by the parchment membrane. The cell was left for 3—6 days, until equilibrium was attained, and the two solutions were then removed and analysed.

The concentration of the casein in the solutions was determined by estimation of the nitrogen content by Kjeldahl's method. The

nitrogen content of the casein having been previously determined, it was possible to calculate the concentration of the casein.

In some cases the concentration was deduced from the dry weight after evaporation. The alkali equivalent of the casein, *i.e.*, the number of equivalents of sodium hydroxide combining with one gram of casein to give a solution neutral to phenolphthalein, agreed with the values given by Sackur (*loc. cit.*) and by Pauli (*loc. cit.*).

The sodium chloride concentration was determined by evaporating a known volume of the solution, heating the horny residue at a dull red heat until the organic matter was destroyed, and then repeatedly extracting the small residue with boiling water. The sodium chloride in this extract was estimated gravimetrically with silver nitrate. The same procedure was adopted with the liquids from both sides of the membrane.

Although the parchment membrane was practically impervious to the casein-ion, in all cases a very small trace of organic matter was found in the liquid originally free from casein. This small amount was probably dissolved from the parchment. There was some osmosis in all cases.

The parchment, before use, was carefully inspected for pinholes and flaws. In spite of this, a number of experiments were spoilt by the breakdown of the membrane.

The results of a number of experiments are given in Tables I and II.

TABLE I.

Sodium Caseinate and Sodium Chloride assumed completely dissociated. Concentrations in grams per litre.

| Expt. No. | Side. | Initial conc. of cas. | Initial conc. of NaCl. | Final conc. Conc. of Na-ions due to Na-cas. | Final conc. Conc. of Na-ions due to NaCl. | Final conc. Total conc. of Na-ions. | Final conc. Conc. of Cl-ions. | Ionic product. |
|---|---|---|---|---|---|---|---|---|
| A | 1 | 18·33 | — | 0·379 | 0·162 | 0·541 | 0·250 | 0·135 |
| | 2 | — | 1·17 | — | 0·270 | 0·270 | 0·417 | 0·113 |
| B | 1 | 10·55 | — | 0·223 | 0·243 | 0·466 | 0·375 | 0·175 |
| | 2 | — | 1·26 | — | 0·311 | 0·311 | 0·480 | 0·150 |
| C | 1 | 11·75 | — | 0·238 | 0·359 | 0·597 | 0·553 | 0·33 |
| | 2 | — | 1·993 | — | 0·428 | 0·428 | 0·660 | 0·28 |
| D | 1 | 14·07 | — | 0·285 | 0·710 | 0·995 | 1·094 | 1·09 |
| | 2 | — | 3·89 | — | 0·799 | 0·799 | 1·232 | 1·00 |
| E | 1 | 12·95 | — | 0·262 | 1·04 | 1·30 | 1·60 | 2·07 |
| | 2 | — | 5·45 | — | 1·14 | 1·14 | 1·70 | 1·99 |
| F | 1 | 10·55 | — | 0·223 | 1·33 | 1·55 | 2·05 | 3·2 |
| | 2 | — | 6·92 | — | 1·41 | 1·41 | 2·17 | 3·1 |
| G | 1 | 11·39 | — | 0·23 | 2·66 | 2·89 | 4·10 | 11·9 |
| | 2 | — | 14·0 | — | 2·73 | 2·73 | 4·20 | 11·5 |

TABLE II.

| Expt. ..... | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| $a$ (Expt.)..... | 0·8 | 0·7 | 0·7 | 0·7 | 0·8 | 0·72 | 0·6 |
| $a$ (Pauli)..... | 0·62 | 0·67 | 0·66 | 0·64 | 0·65 | 0·67 | 0·66 |

It will be seen from Table I that the value of the ionic product [Na][Cl] is always greater on the side of the membrane where the sodium caseinate is present, indicating that the assumption of complete dissociation for sodium caseinate is incorrect.

From the values given, it is possible to calculate the values of the dissociation of sodium caseinate required to make the ionic product the same on both sides of the membrane. The results of this calculation are shown in Table II, and compared with those obtained by Pauli (" Colloid Chemistry of the Proteins," p. 89).

The theory may also be tested by plotting the ratio of the initial concentration of sodium chloride to the initial concentration of the casein against the ratio of the final concentration of sodium chloride on the colloid side of the membrane to that of the sodium chloride on the other side. The resulting curve is smooth, and of the expected shape.

*Summary.*

1. An account is given of experiments illustrating the effect of the presence of sodium caseinate on the distribution of sodium chloride across a parchment membrane.

2. The results are in fair agreement with the theory of membrane equilibrium in its simplest form.

My best thanks are due to Professor Donnan, at whose suggestion and under whose direction this work has been carried out.

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## CCCXII.—*Studies in Electro-endosmosis. Part I.*

By FRED FAIRBROTHER and HAROLD MASTIN.

NUMEROUS researches have been carried out on electro-endosmosis through diaphragms made from powdered materials, using apparatus of many different types. An account of previous work in this direction may be found in " Kapillarchemie," 1922, by Freundlich. Such determinations have, however, been mainly of a comparative nature. Investigators who have attempted to estimate the actual electro-kinetic potential at the solid–liquid interface of a porous diaphragm have, in effect, calculated the potential gradient along

the solid wall from considerations of the total current flow and the resistance of the liquid.

Helmholtz (*Wied. Ann.*, 1879, **7**, 337) used this method to calculate the electro-kinetic potential at a porous earthenware diaphragm from the measurements of Wiedemann (*Pogg. Ann.*, 1856, **99**, 177). He first developed an expression for the case of electro-endosmosis through a single capillary tube of the form

$$u = I\sigma\zeta/4\pi\eta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$u = qE\zeta/4\pi\eta l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $u$ is the amount of liquid transported in unit time through the tube, $\sigma$ and $\eta$ are respectively the specific resistance and the viscosity coefficient of the liquid, $I$ is the current strength, $E$ the total fall in potential between the ends of the tube, $l$ and $q$ are respectively the length and cross section of the tube, and $\zeta$ is the potential between the two parts of the double layer. Helmholtz then assumed the porous earthenware diaphragm to be equivalent to a bundle of fine capillary tubes. According to equation (1), $u$ is independent of the dimensions of the capillaries or diaphragm, so long as the current intensity remains the same; this had been found empirically to be the case by Wiedemann.

It was first pointed out by Pellat (Perrin, *J. Chim. phys.*, 1904, **2**, 601) that the dielectric constant of the double layer was also a factor in the phenomenon, equation (2) becoming then

$$u = qE\zeta\epsilon/4\pi\eta l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\epsilon$ is the dielectric constant.

Similar expressions have been derived by subsequent workers using slightly different lines of argument. Smoluchowski (*Anzeiger Akad. Wiss. Krakau*, 1903, *A*, 182) showed mathematically that the same expression was also valid for the case of a porous diaphragm, as had been assumed by Helmholtz.

The effective cross section, $\Sigma q$, and the length of a porous diaphragm cannot, however, be measured directly. Gyemant (*Z. physikal. Chem.*, 1922, **103**, 260) measured the electro-endosmosis through barium sulphate contained in a U-tube and calculated the electro-kinetic potential in a similar manner to Helmholtz from the current flowing through the system and the specific resistance of the electrolyte. The specific resistance of the liquid, $\sigma$, is, however, the specific resistance of the liquid enmeshed in the capillaries of the diaphragm and is not necessarily the same as that of the liquid in bulk, as assumed by Helmholtz and Gyemant.

There is, indeed, some evidence to show that the two may not be equal. Smoluchowski (*loc. cit.*) predicted that a liquid in a porous

diaphragm would, on account of the "surface current" along the walls of the capillaries, exhibit an additional conductivity, which in the case of a poorly conducting liquid and fine capillaries might even exceed the ordinary conductivity. Stock (*Anzeiger Akad. Wiss. Krakau*, 1912, *A*, 635) confirmed this experimentally for several organic liquids and quartz powder. Smoluchowski considered that, in the case of a good-conducting salt solution, the relative magnitude of this extra surface conductivity would be quite negligible. McBain (*Joint Symposium of Faraday and Physical Societies*, 1921, p. 150) mentions some experiments of Darke on the conductivity of dilute potassium chloride in a quartz capillary which show an increase over the bulk conductivity of the potassium chloride. Some experiments of one of the present authors (F. F.) which it is hoped to publish shortly, also indicate that in certain cases with dilute aqueous electrolytes there is a small difference between the conductivity of the liquid in bulk and the apparent conductivity of the same liquid in a porous diaphragm.

There is also the case, which can by no means be neglected, where the diaphragm is not a perfect insulator, as, for example, carborundum, when the current will also flow through the solid phase. The effect of this will be most marked in very dilute solutions.

To sum up, the calculation of the potential gradient along the walls of the capillaries, which is the driving force of the electro-endosmosis by Ohm's law, from the current flowing through the diaphragm and the resistance of the electrolyte, involves assumptions which it is better to avoid.

The present paper deals with a method of overcoming these difficulties. The method adopted was to measure the potential gradient across the whole diaphragm, having previously determined the magnitude of $q/l$ in the following way. It was assumed, to begin with, that in $N/10$-potassium chloride the surface conductivity is small compared with the bulk conductivity. A similar assumption was made by Stock for 1% sodium chloride. It is not certain that, even in the case of $N/10$-potassium chloride, the surface conductivity is entirely negligible, but it is very probable that it is relatively small.

The diaphragm was first filled with $N/10$-potassium chloride, and a current from two large storage batteries passed through the diaphragm and a large known variable resistance in series with it. By means of a potentiometer, the falls in potential across the diaphragm and across the resistance were measured. The latter gave from Ohm's law the current flowing through the diaphragm. If $C$ be the current, $E$ the potential fall across the diaphragm, $q$ and

$l$ respectively the *effective* cross section and length of the diaphragm, then

$$C = E\kappa q/l \quad \text{or} \quad q/l = C/E\kappa = k$$

where $\kappa$ is the specific conductivity of $N/10$-potassium chloride in the diaphragm. This, as explained above, is taken as equal to the "bulk conductivity."

The ratio $q/l$ = a constant $k$ has, with a given diaphragm, exactly the same value as the same ratio in equation (3).

This method is, in effect, the measurement of the "cell constant" of the porous diaphragm, assuming for the purpose a knowledge of the conductivity of the calibrating liquid.

Experiments showed that with a diaphragm of uniform grain size (about 0·2 mm. average diameter) the powder could be replaced in the apparatus in such a way that $k$ remained constant to about $\pm 1\%$.

## Experimental.

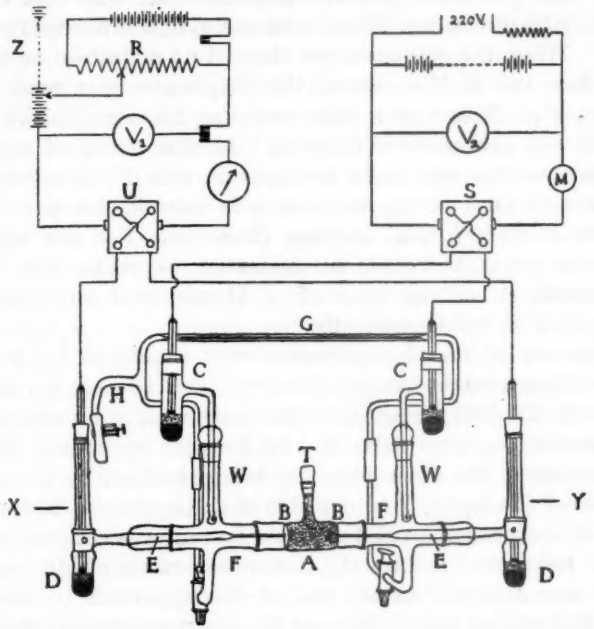
The arrangement of the apparatus may be seen from Fig. 1. The glass parts of the apparatus were fitted together by ground joints, which were kept in position by light metal springs and copper wire collars, and were fixed to a rigid metal rod by two clamps round *FF*, the whole being immersed up to about the level *XY* in an oil thermostat. Second grade medicinal paraffin was used, as, largely on account of the number of ground joints, water gave rise to serious electrical leaks.

*Diaphragm.*—The diaphragm material was contained in a central compartment, *A*, and held in position by disks of silk gauze (bolting silk, 120 mesh) stretched across, and cemented to, the ends of the inside tubes in the joints *BB*, which were ground flat for the purpose. Experiments failed to detect any electro-endosmosis due to the silk gauze; and the cement used, which was not wetted by water, was unaffected by acids or alkalis and did not affect the conductivity of the solutions at all. This method of holding the diaphragm in position permits of a sharp definition of its extremities and is preferable to the use of asbestos or glass wool plugs of indeterminate thickness. The diaphragm material was introduced under water through the side tube, *T*, the apparatus also being filled with water. This obviated the inclusion of air bubbles. The diaphragm was shaken down during filling and allowed to stand over-night. A small reservoir of diaphragm material in *T* was provided to ensure the filling up of any spaces left by subsequent settling; but as a matter of experience there was hardly any later settling.

*External* E.M.F.—The external potential was obtained from a 200-volt battery of small secondary cells which were kept in a

charged condition by the 220-volt lighting mains. A reversing switch, *S*, with an "off" position was included in the circuit and also a micro-ampèremeter, *M*. The potential was applied through the saturated potassium chloride calomel cells, *CC*, and the connecting tubes, which were filled with saturated potassium chloride solution in 5% agar-agar. The lower ends of these tubes were turned up as shown: this device diminished considerably the downward diffusion of potassium chloride.

FIG. 1.




P.D. *across Diaphragm.*—The potential gradient across the diaphragm was measured through the saturated potassium chloride–calomel electrodes, *DD*, and the tubes, *EE*. The latter were drawn out into capillaries of about 0·8 mm. diameter and ground to finish exactly in the plane of the internal joints, *BB*, that is, touching the silk gauze holding the diaphragm. These tubes were filled with water. The cells, *DD*, were made in two portions, fitting together by a ground joint forming a tap, of which the upper tube portion was the hollow plug. The ground joint was lightly greased at the top and bottom, leaving an annular space free from grease; this ring, filled with potassium chloride solution, formed the conducting link between the tube, *E*, and the calomel cell, whilst hindering diffusion of the potassium chloride. The electrical connexions for

the measurement of the potential gradient across the diaphragm are shown on the left of Fig. 1. The potential from the 100-volt battery of small secondary cells, *Z*, could be varied by means of a switch, in steps of approximately 20 volts. The fall of potential across the rheostat, *R*, was about 25 volts and could be arranged in the same, or the opposite direction to the potential from *Z*. Any slight differences of potential between the calomel cells, *DD*, or differences of diffusion potential were negligible in comparison with the *E.M.F.* measured and, further, were eliminated by taking the mean of the potential gradient measurements with the external *E.M.F.* in both directions. The commutator, *U*, was necessary for this purpose. When the galvanometer showed no deflection on depressing the key, the *E.M.F.* across the diaphragm was read on the voltmeter, $V_1$. This was a mirror-reading Siemens-Halske instrument and was calibrated before use. All the electrical measuring apparatus was very well insulated from the rest of the apparatus.

The present form of the apparatus is suitable for powders not finer than about 0·2 mm. average diameter. For use with finer powders or gels, it would be desirable to make the central compartment, *A*, in the form of a U-tube and to arrange the capillary *E.M.F.* tubes vertically.

The amount of liquid transported was measured by a similar means to that used by Briggs, Bennett, and Pierson (*J. Physical Chem.*, 1918, **22**, 256), namely, by the movement of an air bubble in the graduated capillary tube, *G*. In Briggs's apparatus, however, the movement of the air bubble was brought about by the gravitational flow of the liquid from one side of the apparatus to the other, whereas in the present work the liquid system was a closed one, gas evolution being avoided by the use of reversible electrodes. The capillary was attached to the rest of the apparatus by sleeves of thick-walled rubber tube. The air bubble was introduced into the apparatus through the side tube, *H*. The capillary and its associated tubes were kept scrupulously clean and free from grease by frequent washings with acetone and with hot chromic-sulphuric acid mixture. When filling the apparatus with a particular electrolyte solution, the free liquid was run out through the taps and the apparatus rinsed out and filled with the new solution. During the process, the effect of surface tension prevented the liquid from running out of the diaphragm and admitting air bubbles. The diaphragm was then washed through with the liquid, first centrally through the tube *T* and then by passing the liquid through one of the tubes *WW*. The spaces at the ends of the diaphragm were then washed out again and refilled. About 2 litres of solution were used each time : control experiments showed that washing with a further

2 litres did not affect the results appreciably. In all the operations, the solution was introduced into the apparatus by openings which did not come in contact with the oil, and run out by the taps. In spite of these precautions, traces of grease gradually manifested themselves in the lower parts of the apparatus; this was observed when changing the solution, and on its appearance the apparatus was dismantled and cleaned. The grease was never allowed to get anywhere near the diaphragm. The diaphragm was renewed after ten experiments at most. To minimise the introduction of air bubbles into the diaphragm, the solutions were made up with conductivity water which had been boiled and allowed to cool under reduced pressure.

In the determinations given in the present paper, the diaphragm material used throughout was 100-mesh carborundum: other materials are to be examined later. Carborundum was chosen for the first series of experiments for a number of reasons. It is crystalline in nature and unaffected by strong acids: the surface, therefore, can be conveniently purified and freed from grease. It is easily obtainable in quantity, and of a very uniform grain size. Upon the latter very largely depends the possibility of reproducing the packing, that is, the value of $q/l$. One of the principal reasons, however, for the use of carborundum lay in the fact that it offered a means of comparing the electro-kinetic and static potentials of the same substance against electrolyte solutions, carborundum having a small, but quite appreciable, conductivity. The commercial carborundum was heated with aqua regia to remove metallic impurities, with chromic-sulphuric acids to remove carbonaceous matter, and with hydrofluoric acid, in platinum vessels, to remove free silica. It was then washed until the water was quite free from cloudiness, and the surface washed electrically; that is, the carborundum was placed in a U-tube with distilled water and 400 volts was applied between electrodes in the limbs; this was repeated with changes of water until no further electrolysis could be detected.

The purified carborundum was kept under distilled water in order to avoid difficulty with air bubbles, which cling tenaciously to the dry particles. The carborundum was cleaned with chromic-sulphuric acids and electrically washed each time it was removed from the diaphragm chamber.

The electro-endosmosis experiments were carried out as follows. The apparatus, filled with the materials and with the tubes $W$ closed by rubber bungs, was placed in the thermostat with the tube $G$ horizontal and left for 30 minutes, control experiments with a thermometer inserted in the side tube, $T$, so that the bulb was inside the diaphragm, having showed that temperature equilibrium was

attained in 20 minutes. The calomel electrodes, *C*, were placed in position and the electrical connexions completed. On making the circuit, the rate of movement of the bubble in the tube *G* was measured by means of a stop-watch, the potential drop across the diaphragm being measured at the same time. Experience showed that the most concordant results were obtained with a time interval of about 25 seconds : this time is much shorter than that usually measured, but errors due to electrolysis, particularly in the more concentrated solutions, and to gradual changes in the potential drop due to diffusion of potassium chloride from the connecting tubes are greatly minimised thereby. The time was measured repeatedly with the bubble moving in either direction in order to compensate errors due to faulty levelling of the bubble tube. When using conductivity water, as many as fifteen pairs of readings could be made without the value of $\zeta$ dropping appreciably, the error of measurement being less than 1%. The accuracy became considerably less with the more concentrated solutions, and fewer individual readings could be obtained. As a rule, six to eight pairs of readings were averaged to obtain the final result. The sudden drop in $\zeta$ at some point was put down to products of electrolysis reaching the diaphragm; previous investigators have found $\zeta$ to drop very quickly on repeating the measurements several times. Control experiments with a thermometer in the side tube *T* showed that there was no appreciable rise in temperature in the diaphragm during a series of determinations.

The results are given in tabular form below.

TABLE I.

Estimation of the magnitude $q/l$.

| *P.D.* across diaphragm. Volt. | *P.D.* across resistance. Volts. | Resistance. Ohms. | $q/l$. |
|---|---|---|---|
| 0·0415 | 1·238 | 10,000 | 0·255 |
| 0·0475 | 1·147 | 8,000 | 0·252 |
| 0·0546 | 0·9708 | 6,000 | 0·254 |
| 0·0655 | 0·7712 | 4,000 | 0·252 |
| 0·0812 | 0·4770 | 2,000 | 0·251 |

A series of measurements with different packings of the diaphragm gave 0·252 as the mean value of $q/l$.

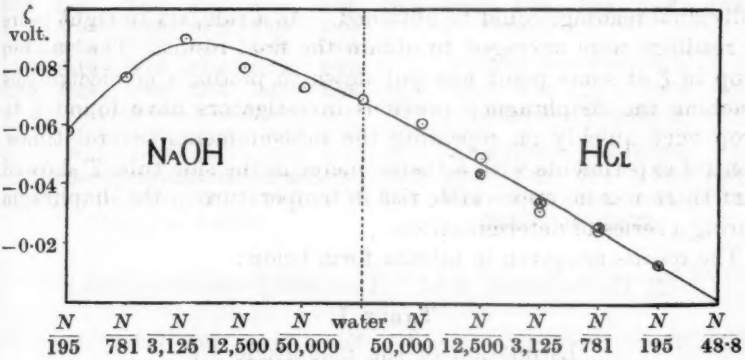
In Table II, "volts" signifies the potential fall across the diaphragm; the time, given in seconds, is the time taken for the air bubble to move through a distance corresponding to a volume $v$, which is given in brackets. $\zeta$ is the electro-kinetic potential calculated according to formula (3), assuming a value of 80 for $\epsilon$ and 0·01006 for $\eta$ and further assuming the absence of slip between the water

and the carborundum. Since further work may require modifications of these assumptions, the experimental data are given in full.

Series of determinations were carried out with both successively increasing and decreasing concentrations of hydrochloric acid in order to establish the fact that a true equilibrium is set up. The latter are marked X in Fig. 2. $\zeta$ is negative in sign.

These results are shown graphically in Fig. 2. It can be seen that the electro-kinetic potential reaches a maximum in dilute alkali and decreases in more concentrated alkaline solutions and in acid solutions. Although the measurements with distilled water are the easiest to carry out, they are least reproducible owing to the rapidity with which the water is contaminated. The value, $\zeta = -0{\cdot}0698$, the mean of fifteen independent determinations, has been adopted.

FIG. 2.




Contrary to the experience of previous workers, no reversal of the direction of flow in acid solution was found for the concentrations used. Perrin (*loc. cit.*) reports such a reversal with carborundum in about $N/125$-hydrochloric acid. Briggs (*loc. cit.*) obtained a marked reversal with his most dilute hydrochloric acid solution, $N/1000$. Neither Briggs nor Perrin indicates the methods he adopted to purify the carborundum. It is felt that the reversal they obtained may have been caused by impurities, possibly carbonaceous, which are known to be present in commercial preparations.

Indications of a reversal have, however, been obtained in $N/25$-hydrochloric acid, though, on account of the relatively large current flowing through the diaphragm, it is difficult to say how far this is due to true electro-endosmosis and how far to electrolytic water transport.

Carborundum may be obtained in two varieties, steely blue

## Table II.

### (1) Hydrochloric Acid. (Increasing concentrations.)

| Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Water ($v$ = 0·4 c.c.). | | | | | | $N$/50000 ($v$ = 0·2 c.c.). | | | | | |
| 105·5 | 33·3 | 6·43 | 105·3 | 34·0 | 6·31 | 54·6 | 33·1 | 6·25 | 54·5 | 34·0 | 6·09 |
| 105·9 | 33·3 | 6·41 | 105·6 | 33·7 | 6·35 | 55·1 | 33·1 | 6·18 | 55·1 | 33·7 | 6·08 |
| 105·4 | 33·4 | 6·42 | 104·9 | 33·7 | 6·39 | 55·5 | 32·9 | 6·18 | 55·1 | 33·4 | 6·14 |
| 104·1 | 33·7 | 6·45 | 104·2 | 34·1 | 6·36 | 55·6 | 33·2 | 6·12 | 56·7 | 33·3 | 5·99 |
| 103·8 | 33·7 | 6·46 | 104·1 | 33·8 | 6·42 | 56·2 | 33·5 | 6·00 | 56·6 | 33·5 | 5·96 |
| 104·0 | 34·5 | 6·30 | 104·0 | 34·3 | 6·33 | 57·0 | 33·3 | 5·95 | 57·4 | 33·0 | 5·96 |
| 103·5 | 34·2 | 6·38 | 104·1 | 34·0 | 6·38 | 58·5 | 32·9 | 5·87 | 57·6 | 33·1 | 5·92 |
| 103·1 | 34·2 | 6·41 | 103·5 | 34·7 | 6·29 | | | | | | |
| 102·5 | 34·5 | 6·39 | 103·2 | 35·2 | 6·22 | | | | | | |
| Mean $\zeta$ = 0·0638. | | | | | | Mean $\zeta$ = 0·0606. | | | | | |
| $N$/12500 ($v$ = 0·1 c.c.). | | | | | | $N$/3125 ($v$ = 0·09 c.c.). | | | | | |
| 41·6 | 26·8 | 5·06 | 40·7 | 27·3 | 5·08 | 40·9 | 39·4 | 3·15 | 40·1 | 39·6 | 3·20 |
| 41·7 | 26·9 | 5·03 | | | | 40·4 | 40·0 | 3·14 | 39·7 | 39·6 | 3·23 |
| 41·7 | 27·5 | 4·92 | 40·7 | 28·5 | 4·87 | 40·7 | 40·0 | 3·12 | 40·7 | 40·2 | 3·11 |
| 42·1 | 27·3 | 4·91 | 40·1 | 28·9 | 4·87 | 40·6 | 40·8 | 3·08 | 39·7 | 40·3 | 3·18 |
| | | | | | | 40·2 | 40·8 | 3·10 | 40·5 | 40·3 | 3·11 |
| | | | | | | 40·5 | 40·5 | 3·10 | 39·7 | 40·6 | 3·16 |
| | | | | | | 39·9 | 41·0 | 3·11 | 38·7 | 41·8 | 3·14 |
| | | | | | | 39·2 | 41·7 | 3·12 | 38·9 | 41·4 | 3·16 |
| Mean $\zeta$ = 0·0496. | | | | | | Mean $\zeta$ = 0·0314. | | | | | |
| $N$/781·2 ($v$ = 0·04 c.c.). | | | | | | $N$/48·8. | | | | | |
| 26·9 | 30·1 | 2·79 | 26·1 | 35·0 | 2·47 | Carborundum distinctly negative. | | | | | |
| 27·0 | 31·5 | 2·66 | 26·8 | 37·9 | 2·22 | | | | | | |
| Mean $\zeta$ = 0·0253. | | | | | | | | | | | |

### (2) Hydrochloric Acid. (Decreasing concentrations.)

| Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. | Volts. | Time. | $\zeta \times 10^3$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $N$/48·8. | | | | | | $N$/781·2 ($v$ = 0·04 c.c.). | | | | | |
| Carborundum distinctly negative. | | | | | | 29·0 | 30·4 | 2·56 | 29·2 | 29·0 | 2·67 |
| | | | | | | 29·6 | 30·2 | 2·53 | 29·0 | 28·6 | 2·72 |
| $N$/195·3 ($v$ = 0·01 c.c.). | | | | | | 29·8 | 31·0 | 2·44 | 29·6 | 27·6 | 2·76 |
| 18·5 | 26·8 | 1·14 | 18·3 | 21·2 | 1·46 | 29·8 | 31·0 | 2·44 | 29·2 | 27·9 | 2·77 |
| 18·2 | 28·1 | 1·10 | | | | 29·7 | 30·8 | 2·47 | 29·2 | 27·5 | 2·81 |
| 18·2 | 28·0 | 1·11 | 17·9 | 20·9 | 1·51 | 29·8 | 30·7 | 2·47 | 29·0 | 28·0 | 2·77 |
| 18·0 | 29·4 | 1·07 | 17·9 | 20·5 | 1·54 | 29·8 | 30·9 | 2·45 | 28·9 | 28·2 | 2 77 |
| 18·0 | 29·1 | 1·08 | 17·7 | 21·2 | 1·50 | 29·8 | 31·3 | 2·42 | 29·4 | 28·1 | 2·74 |
| Mean $\zeta$ = 0·0130. | | | | | | Mean $\zeta$ = 0·0261. | | | | | |
| $N$/3125 ($v$ = 0·05 c.c.). | | | | | | $N$/12500 ($v$ = 0·1 c.c.). | | | | | |
| 31·8 | 24·0 | 3·70 | 32·3 | 26·3 | 3·32 | 40·2 | 32·1 | 4·38 | 40·0 | 31·3 | 4·51 |
| 31·7 | 24·7 | 3·61 | 32·2 | 26·0 | 3·37 | 40·2 | 32·3 | 4·35 | 40·6 | 30·8 | 4·52 |
| 31·8 | 24·9 | 3·56 | 31·8 | 26·2 | 3·39 | 40·2 | 32·1 | 4·38 | 40·8 | 31·0 | 4·46 |
| 31·8 | 24·9 | 3·56 | 32·0 | 26·3 | 3·36 | 40·7 | 32·1 | 4·32 | 40·5 | 30·5 | 4·57 |
| 31·8 | 25·1 | 3·54 | 31·8 | 27·2 | 3·26 | 40·6 | 32·0 | 4·35 | 41·6 | 30·4 | 4·46 |
| 31·1 | 25·0 | 3·63 | 31·8 | 26·6 | 3·34 | 40·7 | 32·5 | 4·27 | 41·7 | 30·4 | 4·45 |
| 31·0 | 25·2 | 3·61 | 31·8 | 26·8 | 3·31 | 40·9 | 31·7 | 4·36 | 42·6 | 29·4 | 4·51 |
| | | | | | | 41·6 | 31·5 | 4·31 | 42·7 | 29·5 | 4·48 |
| | | | | | | 41·7 | 31·1 | 4·35 | 43·6 | 28·8 | 4·50 |
| Mean $\zeta$ = 0·0347. | | | | | | Mean $\zeta$ = 0·0442. | | | | | |

## (3) Sodium Hydroxide.

| Volts. | Time. | $\zeta \times 10^2$. | Volts. | Time. | $\zeta \times 10^2$. | Volts. | Time. | $\zeta \times 10^2$. | Volts. | Time. | $\zeta \times 10^2$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Water ($v$ = 0·3 c.c.). | | | | | | $N/50000$ ($v$ = 0·3 c.c.). | | | | | |
| 87·2 | 34·3 | 5·66 | 90·6 | 33·6 | 5·56 | 65·6 | 34·8 | 7·42 | 68·6 | 34·7 | 7·12 |
| 88·0 | 34·1 | 5·64 | 90·0 | 33·6 | 5·60 | 64·6 | 35·0 | 7·49 | 68·7 | 34·5 | 7·15 |
| 88·9 | 33·3 | 5·72 | 90·9 | 33·4 | 5·58 | 65·3 | 35·4 | 7·33 | 68·6 | 34·6 | 7·14 |
| 88·0 | 33·1 | 5·82 | 90·1 | 33·4 | 5·63 | 64·6 | 35·8 | 7·32 | 67·7 | 34·6 | 7·23 |
| 88·3 | 33·0 | 5·81 | 91·0 | 33·0 | 5·64 | 64·6 | 35·6 | 7·37 | 68·1 | 35·2 | 7·07 |
| 87·8 | 33·4 | 5·78 | 90·3 | 33·6 | 5·58 | 64·1 | 35·9 | 7·36 | 67·6 | 35·6 | 7·04 |
| 88·5 | 32·9 | 5·82 | 91·9 | 31·9 | 5·78 | 63·9 | 35·9 | 7·38 | 67·1 | 35·8 | 7·05 |
| 90·0 | 32·5 | 5·79 | 92·5 | 31·6 | 5·78 | | | | | | |
| Mean $\zeta$ = 0·0570. | | | | | | Mean $\zeta$ = 0·0724. | | | | | |
| $N/12500$ ($v$ = 0·25 c.c.). | | | | | | $N/3125$ ($v$ = 0·2 c.c.). | | | | | |
| 54·6 | 33·0 | 7·83 | 54·6 | 32·0 | 8·08 | 49·1 | 26·6 | 8·65 | 46·1 | 26·4 | 9·28 |
| 57·5 | 31·4 | 7·82 | 57·6 | 30·1 | 8·14 | 49·6 | 26·9 | 8·46 | 45·7 | 26·5 | 9·32 |
| 58·7 | 30·0 | 8·02 | 58·7 | 29·8 | 8·07 | 48·8 | 27·7 | 8·35 | 45·7 | 26·2 | 9·43 |
| 59·2 | 30·1 | 7·92 | 59·1 | 29·7 | 8·04 | | | | 44·7 | 26·6 | 9·50 |
| 59·6 | 30·2 | 7·84 | 59·6 | 29·3 | 8·08 | 47·9 | 27·2 | 8·67 | 46·1 | 26·5 | 9·24 |
| 59·7 | 30·1 | 7·85 | 59·6 | 29·6 | 8·00 | 48·8 | 27·5 | 8·42 | 46·6 | 25·9 | 9·36 |
| | | | | | | 49·6 | 27·2 | 8·37 | 46·8 | 26·4 | 9·14 |
| Mean $\zeta$ = 0·0798. | | | | | | Mean $\zeta$ = 0·0890. | | | | | |
| $N/781·2$ ($v$ = 0·15 c.c.). | | | | | | $N/195·3$ ($v$ = 0·06 c.c.). | | | | | |
| 39·2 | 30·8 | 7·02 | 39·7 | 25·7 | 8·30 | 21·7 | 29·0 | 5·38 | 21·7 | 25·9 | 6·03 |
| 41·8 | 29·4 | 6·89 | 39·9 | 25·8 | 8·23 | 21·6 | 29·0 | 5·41 | 21·5 | 26·0 | 6·06 |
| 42·7 | 28·9 | 6·86 | 39·8 | 25·8 | 8·25 | 21·8 | 29·5 | 5·27 | 21·8 | 25·4 | 6·12 |
| 39·7 | 30·2 | 7·06 | 38·7 | 26·0 | 8·42 | 21·8 | 29·1 | 5·34 | 21·4 | 25·9 | 6·11 |
| 41·1 | 30·4 | 6·78 | 38·7 | 25·9 | 8·45 | 21·8 | 28·9 | 5·38 | 21·4 | 25·8 | 6·14 |
| 40·7 | 29·8 | 6·97 | 39·1 | 26·3 | 8·23 | | | | | | |
| Mean $\zeta$ = 0·0762. | | | | | | Mean $\zeta$ = 0·0574. | | | | | |

crystals and sea-green crystals. Both kinds have been used in the present work and both gave precisely similar results.

A further discussion of the interfacial potential between carborundum and an aqueous electrolyte is reserved for a subsequent paper.

*Summary.*

(1) A method has been developed for the measurement of electro-endosmosis through a diaphragm of powdered material with the simultaneous measurement of the potential gradient across the diaphragm. The ratio of the effective cross section to the effective length of the diaphragm has also been measured electrically.

(2) Measurements have been carried out with carborundum powder in solutions of hydrochloric acid and sodium hydroxide of different concentrations. The electrokinetic potential, calculated from the modified Helmholtz equation, reaches a maximum in dilute alkali, decreasing in more concentrated alkaline solutions and in acid solutions, the carborundum being negatively charged with respect to the water.

— 0·0698 Volt (the mean of fifteen independent determinations) has been adopted as the value for $\zeta$ in distilled water.

(3) Contrary to the experience of other workers, carborundum does not exhibit any reversal of the direction of electro-endosmosis in hydrochloric acid solutions up to $N/50$ strength.

The authors are indebted to Mr. H. E. Martin, M.Sc., for assistance with the preliminary observations and to the Chemical Society Research Fund and the Brunner Mond research grant to this Department for assistance in the above work.

THE UNIVERSITY, MANCHESTER. [*Received, July 22nd,* 1924.]

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## CCCXIII.—*γ-Hydroxystearic Acid.*

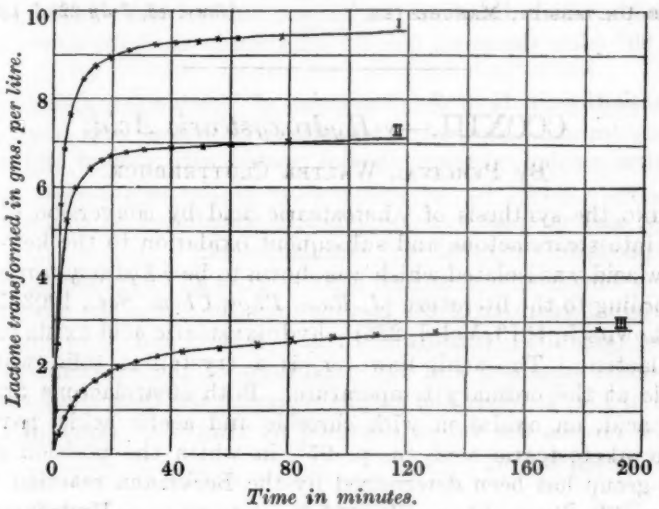
By PERCIVAL WALTER CLUTTERBUCK.

DURING the synthesis of γ-ketostearic acid by conversion of oleic acid into stearolactone and subsequent oxidation to the keto-acid, a new acid was isolated which was shown to be *γ-hydroxystearic acid.* According to the literature (*J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1; Lewkowitsch, 1913, Vol. I, 226) γ-hydroxystearic acid exists only as the lactone. The acid, however, is a crystalline solid which is stable at the ordinary temperature. Both stearolactone and the new acid, on oxidation with chromic and acetic acids, gave the same γ-ketostearic acid, m. p. 97°, in which the position of the keto-group has been determined by the Beckmann reaction on its oxime (*J. Russ. Phys. Chem. Soc., loc. cit.*). γ-Hydroxystearic acid loses 1 mol. of water by heating for 10 minutes at 100°, regenerating stearolactone, m. p. 52—53°.

In view of the interest in sugar chemistry attached to the interconversion of hydroxy-acids and lactones, and for comparison with the classical work of Henry on the interconversion of butyrolactone and γ-hydroxybutyric acid, it was decided to investigate quantitatively the conversion of stearolactone into sodium γ-hydroxystearate and the passage of the hydroxy-acid back into the lactone in presence of hydrogen ions. Henry found that butyrolactone passes spontaneously at the ordinary temperature into an equilibrium mixture of acid and lactone, and, in aqueous solution, this attainment of equilibrium is by a bimolecular reaction; in aqueous solution in presence of hydrogen-ions, the hydroxy-acid passes back into the lactone, the reaction being unimolecular and autocatalysed by the hydrogen ions of the acid itself. Stearolactone, however, does not under ordinary conditions show any

tendency to pass into the γ-hydroxy-acid, nor *vice versa*. Neither the lactone nor the acid, when maintained at 40° for 6 hours in alcoholic solution and titrated periodically, showed any appreciable change. The conversion of lactone into sodium γ-hydroxystearate was bimolecular, the conversion of acid into lactone was unimolecular, and both these reactions went practically to completion. No evidence could be obtained supporting the view that the passage of lactone into acid took place *via* enolisation.

FIG. 1.




For Curve I, $a=9{\cdot}63$, $T=40°$, $aC=0{\cdot}70$.
For Curve II, $a=7{\cdot}12$, $T=40°$, $aC=0{\cdot}70$.
For Curve III, $a=2{\cdot}845$, $T=25°$, $aC=0{\cdot}097$.

γ-Hydroxystearic acid, therefore, can easily be prepared from its salts and appears to be much more stable than γ-hydroxybutyric acid.

## EXPERIMENTAL.

*Preparation of Stearolactone.*—In essentials, the method employed was that of Shukov and Schestakov (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 830). Concentrated sulphuric acid (35 g.) was gradually added, with cooling, to oleic acid (70 g.), the mixture was heated at 80—85° for 6 hours, an equal volume of water added, and the warming continued on a water-bath. The supernatant, viscous oil was separated, washed with brine and with caustic soda solution, and the lactone, extracted therefrom with ether, was washed with methylated spirit, dried, warmed with light petroleum, and

the hydroxy-acid filtered off; the lactone was recovered from the solution and recrystallised from spirit. This process was repeated until the lactone was obtained as a fine, white, crystalline powder, m. p. 52—53° (yield 30%).

*Preparation of γ-Hydroxystearic Acid.*—Stearolactone (10 g.) and an excess of alkali were diluted to about 400 c.c., heated in a boiling-water bath for ½ hour, cooled to about 40°, and acidified with dilute hydrochloric acid. The acid was immediately filtered off, washed with water, dried (yield almost quantitative), and separated from a trace of unchanged lactone by warming with light petroleum, which dissolved the lactone but not the *γ-hydroxy-acid*, m. p. 89° (slow decomp.) (*M*, by titration in alcoholic solution, = 300).

*Quantitative Study of the Conversion of Stearolactone into Sodium Hydroxystearate.*—Equivalent quantities of lactone and base, each in neutral alcohol (absolute alcohol treated with sodium and redistilled), were raised to the temperature of the thermostat, mixed rapidly, and samples were periodically transferred to cold alcohol and immediately titrated with standard acid.

For a bimolecular reaction, $x/t(a - x) = aC$ = constant, where $a$ = original quantity of the lactone (gms./lit.), $x$ = the amount of lactone (gms./lit.) transformed in $t$ mins., and $C$ = constant. The results obtained and the conditions of the experiments are shown in Fig. 1, where the graphs represent the theoretical curves, and the crosses the values obtained by titration. Some of these are tabulated below.

| Expt. 1. $a = 9{\cdot}63$. $T = 40°$. | | | Expt. 2. $a = 7{\cdot}12$. $T = 40°$. | | | Expt. 3. $a = 2{\cdot}845$. $T = 25°$. | | |
|---|---|---|---|---|---|---|---|---|
| $t$. | $x$. | $aC$. | $t$. | $x$. | $aC$. | $t$. | $x$. | $aC$. |
| 2 | 5·62 | 0·70 | 0·75 | 2·48 | 0·71 | 4 | 0·79 | 0·096 |
| 5·5 | 7·63 | 0·69 | 4 | 5·26 | 0·70 | 10 | 1·41 | 0·098 |
| 14 | 8·75 | 0·71 | 7·5 | 5·98 | 0·70 | 19 | 1·86 | 0·099 |
| 25 | 9·12 | 0·71 | 16 | 6·54 | 0·70 | 28 | 2·08 | 0·096 |
| 34 | 9·25 | 0·71 | 24 | 6·72 | 0·70 | 35 | 2·19 | 0·095 |
| 41 | 9·31 | 0·71 | 30 | 6·80 | 0·71 | 44 | 2·30 | 0·096 |
| 55 | 9·39 | 0·71 | 40 | 6·88 | 0·71 | 68 | 2·47 | 0·097 |

*Quantitative Study of the Conversion of γ-Hydroxystearic Acid into Stearolactone.*—γ-Hydroxystearic acid and sulphuric acid, each in alcohol, were raised to the temperature of the thermostat, rapidly mixed, and samples were removed as before and titrated with carbon dioxide-free caustic soda.

For a unimolecular reaction, $k = 1/t.\log a/(a - x)$, where $a$ = original quantity of hydroxy-acid, and $x$ = amount of lactone formed in $t$ mins. The following results were obtained ($a = 3{\cdot}66$; $T = 25°$; 0·05$N$-sulphuric acid):—

| | | | | | |
|---|---|---|---|---|---|
| $t$ ..... | 4 | 7 | 17 | 31 | 39 |
| $x$ ..... | 0·256 | 0·456 | 0·997 | 1·595 | 1·851 |
| $k \times 10^4$ ..... | 79 | 81 | 81 | 80 | 79 |

In conclusion, the author desires to thank Professor H. S. Raper for helpful suggestions and criticism in connexion with this work.

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# CCCXIV.—*Reduction Products of Arylidenecyanoacetic Acids.*

By WILSON BAKER and ARTHUR LAPWORTH.

THE method used by Lapworth and McRae (J., 1922, **121**, 1699) for the synthesis of arylidenecyanoacetic acids has proved so remarkably cheap and convenient that these acids now appear likely to serve as the most satisfactory and economical starting points for the preparation of numerous important aromatic compounds. The work described in the present paper is the outcome of some of the experiments which have been made to test their utility in various directions, and starts from the observation that the arylidenecyanoacetic acids, unlike the corresponding alkylidene compounds (Higginbotham and Lapworth, J., 1923, **123**, 1618), are readily reduced by sodium amalgam and water to the corresponding saturated acids :

$$R{\cdot}CH{:}C(CN){\cdot}CO_2H + 2H \longrightarrow R{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2H.$$

Benzylidene-, anisylidene-, salicylidene-, piperonylidene-, *m*-hydroxybenzylidene-, and 2 : 4-dihydroxybenzylidene-cyanoacetic acids have been reduced in this manner; the yields were 85 per cent. or over, and the process was found to be applicable with large quantities of material. The *cyanoanisylpropionic, cyanosalicylpropionic, cyano*-m-*hydroxyphenylpropionic*, and *cyano*-2 : 4-*dihydroxyphenylpropionic acids* are here described for the first time, as are also the condensations of *m*-hydroxybenzaldehyde and resorcylaldehyde with an aqueous solution of sodium cyanoacetate.

The saturated acids are readily hydrolysed by caustic alkalis to the corresponding malonic acids; and, in general, are converted into the corresponding nitriles on heating with copper powder.

Incidentally it was observed that whilst during the bromination of benzylcyanoacetic acid in water, a partial hydrolysis of the nitrile group took place, in benzene it was accompanied by evolution of carbon dioxide and formation of α-bromo-β-phenylpropionitrile :

$$CH_2Ph{\cdot}CH(CN){\cdot}CO_2H + Br_2 \longrightarrow CH_2Ph{\cdot}CHBr{\cdot}CN + CO_2 + HBr.$$

## EXPERIMENTAL.

(1) *Reduction of α-Cyano-β-phenylacrylic Acid. Benzylcyanoacetic Acid.*—The unsaturated acid is suspended in about four times its weight of water in a separating funnel, and 2 per cent. well-washed sodium amalgam added in small quantities at a time with vigorous shaking, the temperature being kept at about 0°. At the moment that each portion of the amalgam is used up, the liquid for an instant assumes a vivid orange-yellow shade which quickly fades; the mercury is then run off, fresh amalgam introduced, and the process continued. After completion of the reaction the liquid is carefully neutralised, filtered, and an excess of concentrated hydrochloric acid added, when the product separates as an oil, which, on vigorously shaking, rapidly sets to a white, crystalline solid.

By crystallisation from benzene, pure benzylcyanoacetic acid, m. p. 101—102°, is obtained. When heated alone, or, better, with copper powder (see Willstätter and Pummerer, *Ber.*, 1904, **37**, [*B*], 3745; Rinkes, *Rec. trav. chim.*, 1920, **39**, 203), it loses carbon dioxide and yields β-phenylpropionitrile; whilst treatment with cold concentrated sulphuric acid with subsequent pouring on to ice converts it into benzylmalonamic acid, $CH_2Ph{\cdot}CH(CO{\cdot}NH_2){\cdot}COH_2$ (Found: C = 62·2; H = 5·8; equiv. = 192·8. $C_{10}H_{11}O_3N$ requires C = 62·2; H = 5·7%; equiv. = 193·1). This compound crystallises from water in colourless plates or needles which melt at 141° with evolution of carbon dioxide and quantitative formation of β-phenylpropionamide.

*By-product of the reduction.* During one reduction of the unsaturated acid (120 g.) the temperature rose to about 45°, and at the end of the reaction a quantity (24 g.) of a heavy oil separated from the alkaline solution, which readily dissolved in hot alcohol, and on cooling deposited colourless, silky needles (6·9 g.), whilst the mother-liquor contained tarry matter and cinnamonitrile.

This neutral compound separates from alcohol, if growth is slow, in small, highly refracting, pseudo-trigonal prisms, m. p. 171·5° [Found: C = 81·40, 81·68; H = 5·58, 5·62; N = 8·56, 8·60%. *M* (Rast's method, *Ber.*, 1922, **55**, [*B*], 1051) = 332]. It is unaffected by 4 hours' boiling with concentrated hydrochloric acid or 40% sodium hydroxide solution, but is slowly hydrolysed by boiling with potassium hydroxide dissolved in amyl alcohol, ammonia being evolved. It dissolves unchanged in cold concentrated sulphuric acid, but on heating the solution for several hours on the steam-bath and pouring into water, a white, crystalline, neutral compound separates, which is soluble in hot water and melts at

220°, and is probably an acid amide derived by partial hydrolysis of one or more nitrile groups.

The constitution of this by-product has not been established, but from its method of formation and properties it is probably βγ-diphenyladiponitrile ($C_{18}H_{16}N_2$, which requires C = 83·08; H = 6·15; N = 10·8%), since many αβ-unsaturated compounds give bimolecular products when reduced with sodium or aluminium amalgam, but the analyses do not agree well with this substance, and further it is not identical with a bimolecular product obtained by reducing cinnamonitrile with sodium amalgam in dilute alcohol or water. This latter experiment gave, in addition to β-phenylpropionitrile, a compound which separated from the oily reduction product in colourless, silky needles, m. p. 212—212·5°. This experiment does not necessarily exclude the possibility of the by-product being a βγ-diphenyladiponitrile, since the latter is capable of existing in two stereoisomeric modifications, as is βγ-diphenyladipic acid itself and its dimethyl ester (Henle, *Annalen*, 1906, **348**, 16).

The investigation of this substance could not be pursued further, since many attempts to repeat its preparation failed.

(2) *Reduction of α-Cyano-β-anisylacrylic Acid. Formation of α-Cyano-β-anisylpropionic Acid*, $MeO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2H$.—Cyanoanisylacrylic acid was reduced as in case (1), transient, yellow colorations being observed during the reduction, which were more intense than those observed during the preceding reduction. The reduction product was precipitated on acidification as a pale yellow oil which quickly solidified; it was recrystallised from a mixture of benzene and light petroleum.

*α-Cyano-β-anisylpropionic acid* forms small, colourless needles, m. p. 82·5°. It is readily soluble in alcohol, acetone, and in hot benzene, but is almost insoluble in ligroin (Found: C = 64·34; H = 5·72. $C_{11}H_{11}O_3N$ requires C = 64·35; H = 5·41%). Its constitution was established by the production of *p*-methoxybenzylmalonic acid on alkaline hydrolysis, which when recrystallised from water melted at 117° and evolved carbon dioxide at 145° (Friedmann and Gutmann, *Biochem. Z.*, 1910, **27**, 493, give the melting point as 118·5° with decomposition).

(3) *Reduction of α-Cyano-β-salicylacrylic Acid. Formation of α-Cyano-β-salicylpropionic Acid*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2H$.—Cyanosalicylacrylic acid, prepared as described by Haarmann and Reimer (D.R.-P. 189252), was reduced as in case (1). The saturated acid was isolated by extraction with ether, and after removal of the solvent was obtained as a crystalline mass, which was triturated with benzene containing a trace of ether to remove a slight stickiness. It was recrystallised by dissolving in ether, adding about four times

the bulk of warm benzene, filtering, and distilling off the solvents until crystals just began to be deposited. On quickly cooling, the acid was obtained as a white, crystalline powder.

*α-Cyano-β-salicylpropionic acid* forms small, colourless needles, m. p. 138°. It is extremely readily soluble in the common oxygen-containing organic solvents, and almost insoluble in benzene, chloroform, and ligroin. Its aqueous solution gives a violet coloration with ferric chloride (Found: C = 62·95; H = 4·72. $C_{10}H_9O_3N$ requires C = 62·80; H = 4·75%).

(4) *Reduction of α-Cyano-β-piperonylacrylic Acid. α-Cyano-β-piperonylpropionic Acid.*—The reduction was carried out as in case (1); the resulting cyanopiperonylpropionic acid, when recrystallised from ether, melted at 142°, and possessed the properties ascribed to it by Piccinini (*Atti R. Accad. Sci. Torino*, 1904, **39**, 121).

(5) *Preparation and Reduction of α-Cyano-β-(3-hydroxyphenyl)-acrylic Acid. Formation of α-Cyano-β-(3-hydroxyphenyl)-propionic Acid,* $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2H$.—The acrylic acid was prepared in almost quantitative yield by condensing *m*-hydroxybenzaldehyde with an alkaline solution of sodium cyanoacetate after the general method described by Lapworth and McRae (*loc. cit.*), but it was found desirable to keep the mixture at 50° for 1 hour. On acidification the unsaturated acid separated in small, yellow crystals which, when reprecipitated from solution in sodium bicarbonate, melted and decomposed at 226° (compare Fiquet, *Bull. Soc. chim.*, 1901, [iii], **25**, 594).

Cyano-3-hydroxyphenylacrylic acid was reduced as in case (1), the product being isolated by extraction with ether. The syrupy acid thus obtained crystallised on stirring, and the solid mass was crushed and washed with benzene containing a little ether. It was recrystallised from a large volume of boiling benzene, and separated in small clusters of colourless needles, m. p. 105—106°.

*α-Cyano-β-(3-hydroxyphenyl)-propionic acid* is extremely soluble in water, alcohol, ether, ethyl acetate, or acetone, insoluble in ligroin, chloroform, or carbon tetrachloride. Its aqueous solution gives a brownish-purple colour with ferric chloride (Found: C = 62·69; H = 4·79; N = 7·53. $C_{10}H_9O_3N$ requires C = 62·80; H = 4·75; N = 7·33%).

(6) *Preparation and Reduction of α-Cyano-β-(2:4-dihydroxyphenyl)-acrylic Acid. Formation of α-Cyano-β-(2:4-dihydroxyphenyl)-propionic Acid.*—The unsaturated acid was prepared in almost quantitative yield from resorcylaldehyde in the same manner as the preceding acrylic acid. It was precipitated on acidification as small, yellow crystals, which, after reprecipitating from solution

in sodium bicarbonate, melted, when rapidly heated, at 248° (decomp.) (Found: N = 6·81. $C_{10}H_7O_4N$ requires N = 6·83%).

Like the corresponding α-cyano-β-(2-hydroxyphenyl)-acrylic acid (Clarke and Francis, *Ber.*, 1911, **44**, 275), this acid cannot be recrystallised unchanged owing to the ease with which it is converted into 7-hydroxycoumarin-3-carboxylic acid (umbelliferone-3-carboxylic acid). This change takes place on boiling with dilute hydrochloric acid, the solution depositing the umbelliferone on cooling, and on dilution showing the violet fluorescence characteristic of this substance. Its colourless solution in concentrated sulphuric acid shows a violet fluorescence, doubtless also due to the same transformation.

The reduction was carried out as in case (1), the product being obtained by extraction with ether. The syrupy residue crystallised slowly on stirring, and the pasty mass was pressed on to porous earthenware and heated in the steam-oven. This acid has not been obtained pure, since, like many of the α-cyano-β-arylpropionic acids, it is extraordinarily difficult to crystallise, and no solvent, or mixture of solvents was found from which it could be satisfactorily recrystallised (Found: C = 60·34; H = 4·72; N = 6·89; equiv. = 212·8. $C_{10}H_9O_4N$ requires C = 57·94; H = 4·38; N = 6·77 per cent.; equiv. = 207·1).

The impure acid melts at 135—140° with slow evolution of gas. It is extremely soluble in the common oxygen-containing organic solvents; insoluble in benzene, chloroform, or ligroin.

ADDENDUM.

*Bromination of Benzylcyanoacetic Acid.*—Powdered benzylcyanoacetic acid (40 g.) and benzene (100 c.c.) were treated with bromine (36·6 g.) in three portions with gentle agitation. For a short time after the first addition no reaction appeared to take place, then fumes of hydrogen bromide appeared, and suddenly a very vigorous evolution of carbon dioxide and hydrogen bromide set in which ceased in a few minutes. The second and third portions of bromine were then added with an interval for the reaction to cease. After removal of the benzene by distillation, an orange oil was left, which was shaken with a solution of sodium carbonate, extracted with ether, and the solution dried and distilled under diminished pressure. The pure nitrile came over at 137—138°/9—10 mm. Direct estimation of the carbon dioxide evolved during the bromination showed that it was 85 % of that theoretically possible, the rest being lost during the subsequent distillation of the benzene. The yield of the nitrile was over 90 % (Found: N = 6·49; Br = 37·98. $C_9H_8NBr$ requires N = 6·66; Br = 38·05 %).

*α-Bromo-β-phenylpropionitrile* is a very pale yellow oil, $d_{17}^{17}$ 1·438, having a slightly peppery odour, but the vapour of which, when volatilised with steam, is very pungent. It is readily hydrolysed by heating with aqueous sodium hydroxide solution, giving sodium cinnamate, but sodium cyanide may always be detected in solution. Simultaneous reactions no doubt occur according to the scheme:

$$CH_2Ph{\cdot}CHBr{\cdot}CN + 2NaOH \rightarrow \begin{cases} CHPh{:}CH{\cdot}CO_2Na + NaBr + NH_3 \\ CH_2Ph{\cdot}CHO + NaCN + NaBr + H_2O \end{cases}$$

*α-Bromo-β-phenylpropionamide* was prepared from the nitrile by means of a warm alkaline solution of hydrogen peroxide (Radziszewski, *Ber.*, 1885, **18**, 355), and also by dissolving in sulphuric acid and pouring into water. The first method tends to remove hydrobromic acid, giving a mixture of bromophenylpropionamide and cinnamamide. The second method is the better, but the range of conditions which may be used is limited; with sulphuric acid of over 95% strength, the amide tends to lose hydrogen bromide and to undergo further hydrolysis to the carboxylic acid; similar effects result from the use of higher temperatures or longer treatment.

Bromophenylpropionitrile (30 g.) was dissolved in 95% sulphuric acid (200 c.c.), the solution kept at 25° for 40 hours, and then poured into water. After standing, the amide (13 g.) was filtered off, washed with dilute alkali and water, and recrystallised from benzene or hot water, being obtained in small, colourless, nacreous plates, m. p. 128·5° (Found: C = 47·23; H = 4·61; N = 6·16; Br = 34·90. $C_9H_{10}ONBr$ requires C = 47·37; H = 4·42; N = 6·14; Br = 35·09%). It is readily hydrolysed by alkalis, giving cinnamic acid.

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# CCCXV.—*The Interaction between Ethyl Ethylidenemalonate and Anilinophenylacetonitrile.*

By Lucy Higginbotham, Arthur Lapworth, and Charles Simpson.

With a view to extend the synthetic method discovered by Clarke and Lapworth (J., 1907, **91**, 694), anilinophenylacetonitrile (I) has now been allowed to react in presence of alkali with ethyl ethylidenemalonate (II).

$$\begin{array}{lll} \text{(I.)} & C_6H_5\cdot CH(CN)\cdot NHPh & \\ & + & \longrightarrow \quad C_6H_5\cdot C(CN)\cdot NHPh \\ \text{(II.)} & CH_3\cdot CH{:}C(CO_2Et)_2 & \qquad\qquad\quad | \qquad\qquad\quad \text{(III.)} \\ & & \qquad\quad CH_3\cdot CH\cdot CH(CO_2Et)_2 \end{array}$$

It was anticipated that the compound (III) would be formed and that this, by loss of the elements of hydrogen cyanide, would yield the phenylimino-derivative (IV) of ethyl α-[α-benzoylethyl]-malonate (V).

$$\begin{array}{l} C_6H_5\cdot C{:}NPh \\ CH_3\cdot CH\cdot CH(CO_2Et)_2 \\ \text{(IV.)} \end{array} + H_2O \longrightarrow \text{aniline} + \begin{array}{l} C_6H_5\cdot CO \\ CH_3\cdot CH\cdot CH(CO_2Et)_2 \\ \text{(V.)} \end{array}$$

Energetic hydrolysis of (V) would, of course, yield the corresponding dicarboxylic acid (VI) and this by loss of carbon dioxide would give β-benzoylbutyric acid (VII).

$$\begin{array}{ll} \text{(VI.)} & C_6H_5\cdot CO\cdot CH(CH_3)\cdot CH(CO_2H)_2 \\ \text{(VII.)} & C_6H_5\cdot CO\cdot CH(CH_3)\cdot CH_2\cdot CO_2H \end{array} \qquad \begin{array}{l} C(C_6H_5)(CN)\text{—}NPh \\ | \qquad\qquad >CO \\ CH(CH_3)\cdot CH(CO_2Et) \\ \text{(VIII.)} \end{array}$$

Under certain conditions, the reaction led to the formation of a yellow powder, the composition of which agreed roughly with that required for a potassio-derivative of (III), and which, when heated with alkalis, yielded some cyanide and aniline, together with the dicarboxylic acid (VI).

The main products of the reactions, however, were different from those expected, and the anilino-ester (III) was mainly converted into the internal anilide (VIII) with elimination of the elements of ethyl alcohol; the yellow powder was also largely convertible into ethyl 5-cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine-3-carboxylate (VIII), a well-defined, crystalline ester.

The ester (VIII) affords aniline and cyanide only on drastic treatment with strong alkali, the cyanide especially being formed only in small quantity; the other product is the ketonic acid (VI). It is evident from the structure of (VIII) that the elements of aniline or of hydrogen cyanide can only be eliminated after destruc-

tion of the very stable pyrrolidine ring. The first action of alkalis on the compound is to hydrolyse the carboxyethyl group, with formation of the free cyanoketodiphenylmethylpyrrolidinecarboxylic acid (p. 2341). This acid, by loss of the elements of carbon dioxide, is converted into the neutral crystalline 5-cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine. This compound, by drastic treatment with alkalis, yields aniline, cyanide, and β-benzoylbutyric acid (VII), but is converted by sulphuric acid into the amide (XI) of 2-keto-1 : 5-diphenyl-4-methylpyrrolidine-5-carboxylic acid.

Attempts were made to modify the initial reaction so as to preclude the formation of (VIII) and to prepare the *N*-methyl derivative of (III) by the interaction of the *N*-methyl derivative of (I) with the ester (II). Combination of the components was almost entirely inhibited, however, and no product corresponding with (III) could be isolated.

Processes by means of which α-[α-benzoylethyl]-malonic acid (V) and benzoylbutyric acid (VII) can be obtained from the preceding products are mentioned in the practical section. The authors have synthesised these two acids by the following method, which leaves no doubt as to their constitution.

The monobromo-derivative (IX) of phenyl ethyl ketone reacts with ethyl potassiomalonate, yielding the ester (V) :

$$\text{(IX.)}\ \begin{matrix}C_6H_5\cdot CO\\ CH_3\cdot CHBr\end{matrix} + K\cdot CH(CO_2Et)_2 \longrightarrow \begin{matrix}C_6H_5\cdot CO\\ CH_3\cdot CH\cdot CH(CO_2Et)_2\end{matrix} + KBr.$$

The ester prepared in this way gave, on successive hydrolysis and elimination of carbon dioxide, α-[α-benzoylethyl]malonic acid (VI) and β-benzoylbutyric acid (VII), identical with these compounds obtained as previously stated.

The carboxylic acid corresponding with the ester (VIII) readily yields 5-cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine (X), which strong alkalis break up into alkali cyanide, aniline, and β-benzoylbutyric acid (VII). When (X) is hydrolysed by means of sulphuric acid and water, it is converted into 2-keto-1 : 5-diphenyl-4-methylpyrrolidine-5-carboxylamide (XI); in this, the cyano-group is no longer present, no change corresponding with that of (III) to (IV) can take place, and therefore aniline is not eliminated on hydrolysis with alkalis.

$$\text{(X.)}\ \begin{matrix}C(C_6H_5)(CN)\cdot NPh\\ CH(CH_3)\text{——}CH_2\end{matrix}>CO \qquad \begin{matrix}C(C_6H_5)(CO\cdot NH_2)\cdot NPh\\ CH(CH_3)\text{————}CH_2\end{matrix}>CO \ \text{(XI.)}$$

## Experimental.

*Condensation of Anilinophenylacetonitrile with Ethyl Ethylidenemalonate.*—(1) An ice-cold solution of the nitrile (25·5 g.) and the

ester (22·8 g.) in alcohol (30 c.c.) was treated drop by drop with a solution of potassium hydroxide (6·85 g.) in an equal weight of water. After about 5 minutes, a precipitate, A (19·5 g.), appeared. Water was added to the filtrate from this, when a yellow resin, B (5·8 g.), was deposited. The alkaline mother-liquor from B was heated on the water-bath under a reflux condenser for several hours and yielded some neutral material and a resinous acid, D (10·5 g.).

The product A, which contained potassium, was a yellow powder when dry and melted and darkened at 108—111°. It resinised when left in contact with water, was insoluble in ether, petroleum, or carbon disulphide, and when it was ignited in air gave an ash consisting of potassium carbonate. A satisfactory analysis of this product could not be carried out, owing to the nature of its ash, which prevented complete oxidation [Found: K = 10·1. A potassio-derivative of a compound of formula (III) requires K = 9·04 %]. When the material was boiled with 25 % aqueous sodium hydroxide, the steam contained aniline and alcohol, as was shown by the usual tests, and the alkaline residue contained cyanide.

On boiling A with concentrated alcoholic potassium hydroxide for 2 hours, ammonia was evolved and cyanide formed; when the product was worked up for carboxylic acids soluble in ether, an oily acid was obtained consisting almost wholly of β-benzoylethylmalonic acid (VI).

When heated in aqueous acetone or in dilute acetic acid, A (10 g.) gave about 6 g. of *ethyl 5-cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine-3-carboxylate* (VIII), lustrous, colourless prisms, m. p. 99°, from alcohol, which is readily soluble in cold ether or acetone and in hot alcohol or hot light petroleum (Found: C = 72·0; H = 5·6; N = 8·5, 8·0. $C_{21}H_{20}O_3N_2$ requires C = 72·3; H = 5·8; N = 8·0 %). It dissolves in cold concentrated sulphuric acid, being reprecipitated unchanged on addition of water; if heated with concentrated acid, it chars, sulphur dioxide being evolved, and water subsequently produces no precipitate. It is not changed by boiling with dilute hydrochloric acid, but if it is warmed with alcohol and a little concentrated sulphuric acid the odour of ethyl benzoate becomes perceptible.

When this ester was boiled with 25 % aqueous sodium hydroxide, ammonia, aniline, alcohol, and cyanide were formed as well as some sodium benzoylethylmalonate and a somewhat complex mixture in which a small quantity of the cyanoketodiphenylmethylpyrrolidine described later was detected.

*5-Cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine-3-carboxylic acid* was obtained only as a resin (D., above) from the mother-liquor

remaining in condensation (1) above. It gave the same products as the corresponding ester when heated with alkalis; when heated, it softened at about 40° and was completely liquid at 65° (Found : N = 8·0, 8·9. Equiv. = 321, 318. $C_{19}H_{16}O_3N_2$ requires N = 8·8 %; equiv. = 320). Heating for 2 hours with 50 % potassium hydroxide (20 c.c.) converted it into β-benzoylethylmalonic acid (1·2 g. from 3 g.).

*5-Cyano-2-keto-1 : 5-diphenyl-4-methylpyrrolidine* (X) is prepared by boiling the preceding carboxylic acid with hydrochloric acid and purifying the dark-coloured product with alcohol, when silky needles, m. p. 111°, which are difficult to obtain quite colourless, are obtained (Found : C = 77·6, 76·9; N = 10·0, 10·4. $C_{18}H_{16}ON_2$ requires C = 78·2; N = 10·1 %). It is insoluble in aqueous alkalis, dissolves unchanged in cold concentrated sulphuric acid, and when boiled with excess of alcoholic potassium hydroxide yields potassium cyanide, aniline, and an oil from which β-benzoylbutyric acid can be isolated.

*2-Keto-1 : 5-diphenyl-4-methylpyrrolidine-5-carboxylamide*, a finely-crystalline powder (from alcohol), m. p. 193—194°, was made in small quantity by heating the preceding compound with concentrated sulphuric acid (20—30 parts) for 3 hours at 100° and then pouring on to ice (Found : C = 72·5; H = 5·9. $C_{18}H_{18}O_2N_2$ requires C = 73·4; H = 6·1 %).

*α-Benzoylethylmalonic acid* (VI) was prepared from ethylidenemalonic ester in one step as follows :

A solution of anilinophenylacetonitrile (20 g.) and ethyl ethylidenemalonate (18·6 g.) in alcohol (75 c.c.) was treated at 17° with 50 % aqueous potassium hydroxide (2·2 g.). After 2 hours, excess of the potassium hydroxide solution (45·5 g.) was added and the whole boiled under a reflux condenser for 2 hours. The products were worked up for carboxylic acids soluble in ether; the brown oil (18·5 g.) so obtained, when mixed with a little ether, slowly became crystalline and after being triturated with chloroform and drained, formed a white, crystalline powder, m. p. 164—165° (decomp.) (Found : C = 61·2, 60·7; H = 5·1, 4·9; equiv. = 118. A dibasic acid, $C_{12}H_{12}O_5$, requires C = 61·0; H = 5·1 %; equiv. = 118). It dissolves readily in alcohol and in ether; the crystalline form is sparingly soluble in chloroform or benzene, although the resinous form dissolves somewhat freely. The oxime, semicarbazone, and hydrazone could not be prepared in a pure state, some loss of carbon dioxide taking place during the reactions.

*β-Benzoylbutyric acid* (VII) is most readily obtained by heating the preceding acid at 160°. It is usually of waxy consistency, but it separates in minute quantity from a large volume of hot water

in diamond-shaped crystals, m. p. 59—60° (Equiv. = 192. A monobasic acid, $C_{11}H_{12}O_3$, requires equiv. = 192). It dissolves readily in all organic solvents with the exception of petroleum. Its *semicarbazone* separates from alcohol in minute, diamond-shaped plates, m. p. 177—178°, and is sparingly soluble in water but readily in sodium carbonate solution (Found : N = 17·6, 17·6; equiv. = 251. A monobasic acid, $C_{12}H_{15}O_3N_3$, requires N = 16·9 %; equiv. = 249).

Section II. *Alternative Synthesis of β-Benzoylbutyric Acid. Phenyl α-Bromoethyl Ketone* (IX).

Phenyl ethyl ketone (7 g.) was dissolved in dry ether (15 c.c.), and bromine (9 g.) added, at first drop by drop. From the product, about 10 g. of phenyl α-bromoethyl ketone, b. p. 110—112°/4 mm., were obtained as a yellow oil with lachrymatory properties (Found : Br = 37·0. $C_9H_9OBr$ requires Br = 37·5 %).

The bromoketone (4·5 g.) was added to a suspension of ethyl *potassio*-malonate made from potassium (1 g.) and ethyl malonate (4·5 g.) in dry benzene, and the whole warmed on the water-bath for 6 hours. The resulting ester was hydrolysed by boiling with alcoholic potassium hydroxide, and the product worked up, yielding 3 g. of carboxylic acids soluble in ether. These acids readily solidified completely (the solid melting at about 160°) and consisted almost wholly of α-benzoylethylmalonic acid, identical with the acid obtained by the process described on p. 2342.

In another condensation of the bromoketone with ethyl *sodio*-malonate in alcoholic solution, equally satisfactory results were obtained. The equivalent of the benzoylethylmalonic acid was 118, the theoretical value.

*Action of Alkalis on* N-*Methylanilinophenylacetonitrile.*—On repeating process (1), (p. 2340), but using *N*-methylanilinophenylacetonitrile in place of the non-methylated compound, a non-acid solid (6·9 g.) was obtained, whilst the aqueous solution contained cyanide and the potassium salt of a brown, oily acid.

The non-acid, neutral solid substance, which is also obtained simply by boiling *N*-methylanilinophenylacetonitrile with alkali, formed pale yellow crystals (from alcohol), m. p. 126—128°. It was insoluble in water or dilute alkalis even on boiling; on prolonged treatment with strong alkalis, it gave no soluble cyanide. It had basic properties, being converted into a sparingly soluble compound, doubtless a hydrochloride, by hydrochloric acid, by hydrogen chloride in ether, or by benzoyl chloride; when heated, this product began to decompose at 230° and melted and decomposed completely at 242—244°; when warmed with alkalis, it was recon-

verted into the original non-acid solid. The true nature of the substance has not been determined (Found : C = 74·7, 75·1, 74·7; H = 6·5, 6·5, 6·4; N = 6·0, 6·1. $C_{15}H_{15}O_2N$ requires C = 74·7; H = 6·3; N = 5·8 %).

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## CCCXVI.—*The Influence of Catalysts on Carbonisation.*

By RUDOLF LESSING and MAURICE ALFRED LISTER BANKS.

ATTENTION was directed by one of us to the rôle played by the mineral constituents in the carbonisation of coal (William Young Memorial Lecture, *J. Gas Lighting*, 1914, **127**, 570). Work on this subject in hand in 1914 had to be abandoned on the outbreak of war. We have resumed this investigation with the object of ascertaining the effect of individual compounds on the carbonisation of coal.

Recent investigations by one of us (J., 1920, **117**, 256) showed considerable differences in the composition of the mineral constituents of the four main ingredients of bituminous coal, differences which have since been found typical for each coal constituent (Lessing, *Trans. Inst. Min. Eng.*, 1923, **64**, 296; Baranov and Francis, "Fuel," 1922, **1**, 219). One of the objects of our investigation was to trace the influence of the typical ash on the peculiar behaviour on carbonisation of fusain, durain, clarain, and vitrain, described in a previous paper (J., 1920, **117**, 247).

The difficulty of studying the catalytic effect of individual inorganic compounds is that the original coal ash cannot be reduced below a certain minimum, which is for the four ingredients, when freed from each other and from the accompanying dirt by purely physical means, of the following order of magnitude : Vitrain 0·8—1·5%, clarain 1—3%, durain 5—7%, fusain 10—16%. A further reduction can be made by treatment with acid (Lessing, *loc. cit.*).

The catalytic effect of any added substance must be influenced or obscured by these residual mineral constituents. They are mixtures of carbonates, silicates, and sulphides of alkalis, alkaline earths, and other metals, and possibly organic salts of these.

As coal entirely free from ash is not available, it was thought

advisable in the first instance to resort to other substances which, on thermal decomposition in the absence of air, also yield a coke or char.

For the first series of experiments, pure refined sucrose and cellulose in the form of filter-paper were chosen. A specially prepared sample of sugar was kindly supplied by Messrs. Tate and Lyle, Ltd. According to this firm's statement it contained 0·005% of ash, principally consisting of organic salts of potassium and sodium, probably acetates and malates, with traces only of calcium, chloride, and sulphate.

The cellulose was used in the form of filter-paper, Whatman's No. 42, containing when dry approximately 0·01% of ash.

The addition of inorganic compounds to these substances was made in such small proportions that they could not be expected to act physically as mere inert "fillers." The normal amount was of the order of 1%. However, instead of using equal quantities of all compounds, the additions were made in molecular proportions, on the basis of 0·01 gram-molecule per 100 grams of sugar or filter-paper. In certain instances, definite multiples or fractions were used in order to compare different compounds according to valency. This was done with the object of providing definite data in case stoicheiometric relations were found to exist in the reactions brought about by the reagents or catalysts added.

Various methods of procedure for the admixture of catalysts were tried. Stock mixtures could not be prepared, as a large number of carbonising experiments (amounting to over 450) had to be carried out, and as absolutely homogeneous mixing was not considered feasible.

For accurate dosing, it was found necessary to employ standard solutions, or suspensions, of the reagents. Anticipating that differences would be shown according to whether the reagents were admixed in the dry state or in solution, since the ratio of water to sugar or cellulose was about 1 : 1, "wet" and "dry" experiments were carried out in all cases. About forty reagents were examined. These were selected in the first instance with a view to their basic or acid radicals being present in coal, but a number of others were included, as representing types of compounds likely to have an effect. The list is entirely arbitrary and will be supplemented by other reagents.

It was originally intended to carbonise under conditions which would allow of the estimation of the yield of volatile products, *i.e.*, gas, tar, and aqueous condensate, and a number of experiments have been made on these lines in the coking apparatus designed by one of us (Fuel Research Board, Interim Report on

"Methods of Analysis of Coal," 1923, 21). This scheme was, however, found to be somewhat too ambitious and in order to save time the simpler course was adopted in the first instance of carrying out the tests by heating the mixture in a platinum crucible under standard conditions, but for 3 minutes only instead of the 7 minutes customary in coal analysis, so as to avoid excessive oxidation. The rate of combustion likely to take place is shown by the following test: 1 gram of sugar mixed with 1 c.c. of aqueous solution containing 0·0106 g. of sodium carbonate was heated in a covered platinum crucible at 925° for 1 minute, cooled, and weighed. Heating was repeated for 1 minute several times with the following results:

| Time (mins.) ... | 1 | 2 | 3 | 4 | 5 | |
|---|---|---|---|---|---|---|
| Ash-free coke ... | 13·98 | 13·50 | 13·02 | 12·60 | 12·04 | |
| Loss% ..... | — | 0·48 | 0·48 | 0·42 | 0·56 | Mean 0·48 |

A slight contraction of the coke occurred after the second minute. The 3 minute test is therefore justified.

Instead of stating the results in the usual way in form of "Volatile Matter," the more rational method of returning the actual coke yield obtained was adopted. For comparing the coke yield it was found necessary to deduct from the total coke obtained, that amount of inorganic matter which was derived from the added reagent. This would mostly be different from the compound actually added. In some cases the composition of the residual inorganic matter is practically certain, in others it had to be assumed. Ash analyses were made in some cases. This could not be done always, as the cokes obtained were required for examination of their physical structure. Moreover, the customary form of expressing as "ash-free" matter the coal or coke from which the residue obtained on ignition has been deducted is fundamentally wrong, where mineral constituents are converted into others by oxidation or decomposition in the course of ash estimation. In most cases, likely alternatives for the "compound formed" do not affect the coke yield as regards its quantitative composition in the list.

*Discussion of Results.*

In Tables I and II, results of the experiments with sugar and cellulose respectively are recorded. They are arranged in order of the means of the "wet" and "dry" percentages of coke free from the inorganic additions or the "compounds formed" from them.

Forty compounds were tested and the coke yield was found to vary between 18·74% and 5·02% in the case of sugar, and between 20·36% and 5·10% in the case of cellulose.

TABLE I.

*Influence of Catalysts on the Carbonisation of Sugar.*

| Compound added. | | Compound formed. | | Coke obtained (less "compound formed"). Gms. per 100 gms. of sugar. | | | |
|---|---|---|---|---|---|---|---|
| Formula. | Gms. per 100 gms. of sugar. | | Gms. per 100 gms. of sugar. | Wet. | Dry. | Diff. | Mean. |
| $H_2SO_4$ | 0·98 | — | nil | 18·28 | 18·74 | −0·46 | 18·51 |
| $MgCl_2$ | 0·95 | MgO | 0·40 | 17·89 | 16·96 | +0·93 | 17·43 |
| $CuSO_4$ | 1·60 | $Cu_2S$ | 1·59 | 19·11 | 14·82 | +4·29 | 16·97 |
| $\frac{2}{3}Al_2(SO_4)_3$ | 2·30 | $Al_2O_3$ | 0·68 | 19·35 | 13·67 | +5·68 | 16·51 |
| $AlCl_3$ | 1·34 | $Al_2O_3$ | 0·51 | 17·41 | 15·51 | +1·90 | 16·46 |
| $\frac{1}{2}Al_2(SO_4)_3$ | 1·14 | $Al_2O_3$ | 0·34 | 16·43 | 15·78 | +0·65 | 16·11 |
| $3NH_4Cl$ | 1·61 | — | nil | 16·90 | 15·15 | +1·75 | 16·03 |
| $FeCl_3$ | 1·62 | FeO | 0·72 | 17·02 | 14·44 | +2·58 | 15·73 |
| $\frac{1}{3}Al_2(SO_4)_3$ | 0·57 | $Al_2O_3$ | 0·17 | 15·95 | 12·11 | +3·84 | 14·03 |
| $FeSO_4$ | 1·52 | FeS | 0·88 | 14·00 | 12·46 | +1·64 | 13·23 |
| $\frac{1}{2}FeSO_4$ | 0·76 | FeS | 0·44 | 14·99 | 10·21 | +4·78 | 12·60 |
| 2NaCl | 1·17 | $Na_2CO_3$ | 1·06 | 12·42 | 10·79 | +1·63 | 11·61 |
| $NH_4Cl$ | 0·53 | — | nil | 12·33 | 10·22 | +2·11 | 11·28 |
| $Ni(NO_3)_2$ | 1·83 | NiO | 0·76 | 10·45 | 11·77 | −1·32 | 11·11 |
| $2KNO_3$ | 2·02 | $K_2CO_3$ | 1·38 | — | 11·08 | ? | — |
| $Cu(OH)_2$ | 0·98 | $Cu_2O$ | 1·43 | 11·41 | 10·39 | +1·02 | 10·90 |
| $NaHSO_4$ | 1·20 | $Na_2SO_4$ | 0·71 | 9·97 | 10·94 | −0·97 | 10·46 |
| $Na_2SiO_3$ | 1·22 | $Na_2SiO_3$ | 1·22 | 11·00 | 9·90 | +1·10 | 10·45 |
| $Na_2CO_3$ | 1·06 | $Na_2CO_3$ | 1·06 | 10·18 | 10·69 | −0·51 | 10·44 |
| $K_2CO_3$ | 1·38 | $K_2CO_3$ | 1·38 | 9·08 | 11·19 | −2·11 | 10·14 |
| 2NaOH | 0·80 | $Na_2CO_3$ | 1·06 | 10·89 | 9·17 | +1·72 | 10·03 |
| NaCl | 0·59 | $Na_2CO_3$ | 0·53 | 8·70 | 10·47 | −1·77 | 9·59 |
| $\frac{1}{4}Al_2O_3$ | 0·51 | $Al_2O_3$ | 0·51 | 9·44 | 7·45 | +1·99 | 8·45 |
| $MgSO_4$ | 1·20 | MgO | 0·40 | 8·78 | 7·89 | +0·89 | 8·34 |
| $Al(OH)_3$ | 0·78 | $Al_2O_3$ | 0·51 | 8·09 | 7·74 | +0·35 | 7·92 |
| $CaCO_3$ | 1·00 | CaO | 0·56 | 8·44 | 6·92 | +1·52 | 7·88 |
| $SiO_2$ | 0·60 | $SiO_2$ | 0·60 | 8·26 | 6·93 | +1·33 | 7·61 |
| $MnSO_4$ | 1·51 | MnO | 0·71 | 8·48 | 6·76 | +1·72 | 7·61 |
| China clay | 2·59 | Ign. clay | 2·23 | 8·72 | 6·16 | +2·56 | 7·44 |
| $(NH_4)_2CO_3$ | 0·96 | — | nil | 6·88 | 7·04 | −0·16 | 6·96 |
| $Fe(OH)_3$ | 1·07 | $Fe_2O_3$ | 0·80 | 8·27 | 5·53 | +2·74 | 6·90 |
| $\frac{1}{2}Fe_2O_3$ | 0·80 | $Fe_2O_3$ | 0·80 | 7·31 | 6·40 | +0·91 | 6·85 |
| Untreated | nil | — | nil | 6·45 | 6·48 | −0·03 | 6·46 |
| $Na_2SO_4$ | 1·42 | $Na_2SO_4$ | 1·42 | 7·11 | 5·67 | +1·44 | 6·39 |
| FeS | 0·88 | FeS | 0·88 | 6·07 | 6·55 | −0·48 | 6·31 |
| $NiCO_3$ | 1·19 | NiO | 0·75 | 7·28 | 5·26 | +2·02 | 6·27 |
| CaO | 0·56 | CaO | 0·56 | 6·38 | 6·11 | +0·27 | 6·25 |
| $\frac{1}{2}(COOH)_2$ | 0·45 | — | nil | 5·44 | 6·44 | −1·00 | 5·94 |
| CuO | 0·79 | CuO | 0·79 | 6·17 | 5·35 | +0·82 | 5·76 |
| MgO | 0·40 | MgO | 0·40 | 5·62 | 5·26 | +0·36 | 5·44 |
| NiO | 0·75 | NiO | 0·75 | 5·63 | 5·02 | +0·61 | 5·33 |

In most cases, a number of experiments were made with each added compound, the discrepancies between individual tests being within the experimental error, or, at any rate, so small as not to affect the position in the list.

An attempt was made to place the results in groups in order to ascertain the principle which controlled the yield of coke. By

## TABLE II.

*Influence of Catalysts on the Carbonisation of Cellulose.*

| Compound added. Formula. | Gms. per 100 gms. of cellulose. | Compound formed. | Gms. per 100 gms. of cellulose. | Coke obtained (less "compound formed"). Gms. per 100 gms. of cellulose. Wet. | Dry. | Diff. | Mean. |
|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | 0·98 | — | nil | 19·82 | 20·36 | −0·54 | 20·09 |
| $\frac{2}{3}Al_2(SO_4)_3$ | 2·30 | $Al_2O_3$ | 0·68 | 14·77 | 15·11 | −0·34 | 14·94 |
| $CuSO_4$ | 1·60 | $Cu_2S$ | 1·59 | 12·68 | 14·81 | −2·13 | 13·75 |
| $AlCl_3$ | 1·34 | $Al_2O_3$ | 0·81 | 13·07 | 14·36 | −1·29 | 13·72 |
| $\frac{1}{3}Al_2(SO_4)_3$ | 1·14 | $Al_2O_3$ | 0·34 | 12·80 | 14·30 | −1·50 | 13·56 |
| $Na_2CO_3$ | 1·06 | $Na_2CO_3$ | 1·06 | 14·87 | 12·14 | +2·73 | 13·51 |
| $Na_2SiO_3$ | 1·22 | $Na_2SiO_3$ | 1·22 | 13·38 | 13·28 | +0·10 | 13·33 |
| $FeCl_3$ | 1·62 | FeO | 0·72 | 11·78 | 14·80 | −3·02 | 13·29 |
| 2NaOH | 0·80 | $Na_2CO_3$ | 1·06 | 13·46 | 12·84 | +0·62 | 13·15 |
| $MgCl_2$ | 0·95 | MgO | 0·40 | 10·83 | 13·73 | −2·90 | 12·18 |
| NaCl | 0·59 | $Na_2CO_3$ | 0·53 | 12·21 | 11·56 | +0·65 | 11·89 |
| $3NH_4Cl$ | 1·61 | — | nil | 9·92 | 13·50 | −3·58 | 11·71 |
| 2NaCl | 1·17 | $Na_2CO_3$ | 1·06 | 12·65 | 10·64 | +2·01 | 11·65 |
| $K_2CO_3$ | 1·38 | $K_2CO_3$ | 1·38 | 10·98 | 11·55 | −0·57 | 11·27 |
| $2KNO_3$ | 2·02 | $K_2CO_3$ | 1·38 | 9·33 | 12·94 | −3·61 | 11·24 |
| $\frac{1}{2}FeSO_4$ | 0·76 | FeS | 0·44 | 9·64 | 12·07 | −2·43 | 11·08 |
| $FeSO_4$ | 1·52 | FeS | 0·88 | 9·72 | 11·92 | −2·20 | 10·82 |
| $NH_4Cl$ | 0·53 | — | nil | 8·44 | 11·46 | −3·02 | 9·96 |
| $\frac{1}{6}Al_2(SO_4)_3$ | 0·57 | $Al_2O_3$ | 0·17 | 8·37 | 11·38 | −3·01 | 9·88 |
| CuO | 0·79 | CuO | 0·79 | 7·79 | 10·25 | −2·46 | 9·02 |
| $NiCO_3$ | 1·19 | NiO | 0·76 | 8·32 | 9·50 | −1·18 | 8·91 |
| $Na_2SO_4$ | 1·42 | $Na_2SO_4$ | 1·42 | 7·75 | 9·92 | −2·17 | 8·84 |
| $Fe(OH)_3$ | 1·07 | $Fe_2O_3$ | 0·80 | 8·50 | 9·06 | −0·56 | 8·78 |
| CaO | 0·56 | CaO | 0·56 | 8·49 | 9·04 | −0·55 | 8·77 |
| NiO | 0·75 | NiO | 0·76 | 8·55 | 8·82 | −0·27 | 8·69 |
| $Al(OH)_3$ | 0·78 | $Al_2O_3$ | 0·51 | 8·11 | 9·26 | −1·15 | 8·69 |
| $Ni(NO_3)_2$ | 1·83 | NiO | 0·76 | 8·55 | 7·07 | +1·48 | 7·81 |
| $\frac{1}{2}Fe_2O_3$ | 0·80 | $Fe_2O_3$ | 0·80 | 9·03 | 6·11 | +2·92 | 7·57 |
| $Cu(OH)_2$ | 0·98 | $Cu_2O$ | 1·43 | 8·49 | 6·07 | +2·42 | 7·28 |
| $MgSO_4$ | 1·20 | MgO | 0·40 | 6·72 | 7·80 | −1·08 | 7·26 |
| China clay | 2·59 | Ign. clay | 2·23 | 7·88 | 6·51 | +1·37 | 7·20 |
| $\frac{1}{2}Al_2O_3$ | 0·51 | $Al_2O_3$ | 0·51 | 6·92 | 7·24 | −1·32 | 7·08 |
| $NaHSO_4$ | 1·20 | $Na_2SO_4$ | 0·71 | 5·88 | 8·19 | −2·31 | 7·04 |
| MgO | 0·40 | MgO | 0·40 | 5·15 | 7·74 | −2·59 | 6·99 |
| FeS | 0·88 | FeS | 0·88 | 7·27 | 6·51 | +0·76 | 6·89 |
| $MnSO_4$ | 1·51 | MnO | 0·71 | 5·10 | 8·50 | −3·40 | 6·80 |
| $SiO_2$ | 0·60 | $SiO_2$ | 0·60 | 6·70 | 6·85 | −0·15 | 6·78 |
| $(NH_4)_2CO_3$ | 0·96 | — | nil | 4·70 | 8·00 | −3·30 | 6·35 |
| $CaCO_3$ | 1·00 | CaO | 0·56 | 6·20 | 5·63 | +0·57 | 5·92 |
| Untreated | | — | nil | 5·60 | 6·00 | −0·40 | 5·80 |
| $\frac{1}{2}(COOH)_2$ | 0·45 | — | nil | 5·23 | 5·16 | +0·07 | 5·19 |

taking coke yields of 12% and 9% as tentative limits, the results arranged themselves in three main groups, with possibly sub-groups, divided by the 8% line in the case of cellulose. In general, the compounds arrange themselves in like order in the sugar and the cellulose series, although there are some notable exceptions, such

as the high position of sodium carbonate, silicate, and hydroxide in the cellulose series.

Into the highest group fall salts of strong acids and weak bases; the lowest group consists of compounds which do not change the coke yield very appreciably, whilst the middle group consists of a puzzling combination of alkalis and metallic salts with no obvious rational connection.

The untreated substance is practically at the bottom of the list. Oxalic acid, the only organic compound added, produces alone a lower coke yield from cellulose. In the case of sugar, it shares this distinction with the oxides of copper and nickel, and curiously also with lime and magnesia. Apart from these quantitatively unimportant exceptions, it may be said that any compound which acts at all, does so in the direction of an increase in the coke yield.

Whether the action is a truly catalytic one cannot be decided on the evidence so far obtained, and definite proof seems difficult, since the great majority of the chemical reactions involved in carbonisation are irreversible. The small quantity, however, needed for influencing the carbonising equilibrium towards the formation of solid or volatile products of thermal decomposition points to their acting as catalysts.

At the same time, it is quite likely that the added compounds undergo definite reactions, along stoicheiometric lines, with equivalent quantities of the carbohydrates, and that the type of reaction thus initiated, such as hydrolysis, scission of groups, or opening of rings, influences the course of carbonisation in the direction of a higher or lower coke yield.

Experiments are in hand, but not yet concluded, to find whether the directional action of the catalysts consists mainly in the formation of intermediate products, yielding different percentages of coke during subsequent stages of carbonisation, or whether the influence of the catalysts extends to the reactions taking place at these later high-temperature stages of carbonisation.

The remarkable quantitative variation in the yield of coke is equalled, if not surpassed, by the extraordinary differences in appearance and structure shown.

The chars obtained from filter-paper, not having passed through a state of fusion, and having preserved their rigidity, do not differ appreciably in their appearance. The sugar cokes, however, exhibit very considerable and characteristic distinctions. The most striking property is the varying degree of swelling produced by different additions. For the purpose of comparison, the sugar cokes were arranged in three groups: compact, swelled, and flaky, with the result given in Table III.

TABLE III.

| Wet method. | | | Dry method. | | |
|---|---|---|---|---|---|
| Compact. | Swelled. | Flaky. | Compact. | Swelled. | Flaky. |
| $MgCl_2$ | $H_2SO_4$ | $\frac{1}{2}Al_2O_3$ | $MgCl_2$ | $H_2SO_4$ | $\frac{1}{2}Al_2O_3$ |
| $AlCl_3$ | $CuSO_4$ | $MgSO_4$ | $CuSO_4$ | $\frac{1}{2}Al_2(SO_4)_3$ | $MgSO_4$ |
| $3NH_4Cl$ | $Al_2(SO_4)_3$ | $Al(OH)_3$ | $Al_2(SO_4)_3$ | $FeSO_4$ | $Al(OH)_3$ |
| $NH_4Cl$ | $\frac{1}{2}Al_2(SO_4)_3$ | $CaCO_3$ | $AlCl_3$ | $2NaCl$ | $CaCO_3$ |
| $Na_2SiO_3$ | $FeCl_3$ | $SiO_2$ | $3NH_4Cl$ | $2KNO_3$ | $SiO_2$ |
| | $\frac{1}{2}Al_2(SO_4)_3$ | $MnSO_4$ | $FeCl_3$ | $NaHSO_4$ | $MnSO_4$ |
| | $FeSO_4$ | Clay | $\frac{1}{2}Al_2(SO_4)_3$ | $NaCl$ | Clay |
| | $\frac{1}{2}FeSO_4$ | $(NH_4)_2CO_3$ | $\frac{1}{2}FeSO_4$ | | $(NH_4)_2CO_3$ |
| | $2NaCl$ | $Fe(OH)_3$ | $NH_4Cl$ | | $Fe(OH)_3$ |
| | $Ni(NO_3)_2$ | $\frac{1}{2}Fe_2O_3$ | $Ni(NO_3)_2$ | | $\frac{1}{2}Fe_2O_3$ |
| | $2KNO_3$ | Untreated | $Cu(OH)_2$ | | Untreated |
| | $Cu(OH)_2$ | $Na_2SO_4$ | $Na_2SiO_3$ | | $Na_2SO_4$ |
| | $NaHSO_4$ | $FeS$ | $Na_2CO_3$ | | $FeS$ |
| | $Na_2CO_3$ | $CaO$ | $K_2CO_3$ | | $CaO$ |
| | $K_2CO_3$ | $(COOH)_2$ | $2NaOH$ | | $(COOH)_2$ |
| | $2NaOH$ | $CuO$ | | | $CuO$ |
| | $NaCl$ | $MgO$ | | | $MgO$ |
| | | $NiO$ | | | $NiO$ |

The main distinction is between the "wet" and "dry" series. The majority of the catalysts producing high or medium high coke yields make swelled cokes when sugar is carbonised with its own weight of water, and compact cokes when dry sugar is heated. Notable exceptions are compact cokes with most chlorides and sodium silicate by the wet method, and swelled cokes with sulphuric acid, sulphates, sodium chloride, and potassium nitrate by the dry method. Potassium nitrate produces such violent swelling in the early stages of heating, that it was found impossible to obtain a quantitative coke yield by the wet method. Pure sugar, or sugar mixed with compounds not causing an increase in the coke yield, invariably gave a flaky coke.

Differences are not restricted to the general shape of the coke buttons, but they extend to the surface structure, colour, iridescence, brightness and, to judge by shape and weight, also to density and true porosity. Thus, brightness is enhanced by chlorides and nitrates, but alkalis give a dull sooty surface by the dry method, and woolly, gossamer-like excrescences by the wet. Sodium sulphate gives a dull grey surface not shown by any other compound, modified somewhat by swelling in the case of the acid sulphate. These are only examples of discernible characteristics which do not lend themselves to brief description.

The change which the various compounds undergo during the heating process makes it uncertain whether the original salt, base or acid or their intermediate or final products of decomposition are the actual catalysts.

Interpretation of the results is further complicated by lack of

definite knowledge of the behaviour, when heated to 900—950° in contact with an excess of organic matter, of many of the compounds tried. In a number of cases a cursory investigation was made. For instance, the practically complete decomposition of ferric chloride and aluminium chloride was proved, only a small portion being volatilised. The final removal of chlorine from the chlorides of alkalis was also established, confirming the results of Davies (*J. Soc. Chem. Ind.*, 1901, **20**, 98). The sulphates of the alkalis, on the other hand, were found to remain stable, sodium sulphate giving only a small percentage of alkaline ash, whilst no alkaline reaction could be traced in the ash from coke made with sodium hydrogen sulphate. This slight difference illustrates the difficulty due to the fact that the effect of the admixture of salts is the balance of influences of their bases and acids. Their respective strengths and the total amount added determine the position of each catalyst in the list.

The results, as far as sugar is concerned, throw some light on certain phenomena of its combustion. In the discussion of a paper by the late Sir George Beilby (*J. Soc. Chem. Ind.*, 1922, **41**, 341T), one of us suggested that the well-known trick of burning a lump of sugar contaminated with a speck of tobacco ash is due to the initial production of some coke different in character from the product of heating pure sugar in a flame. The present results furnish the definite proof for this contention. Under the influence of the alkalis of tobacco ash, a dull porous coke is produced at a corner of the lump of sugar which acts as a rigid and permeable wick for the ready release of gases from the interior, whilst the pores of the uncontaminated lump are blocked by fused caramel. The results obtained on this point by Hedvall (*Svensk Kem. Tidskrift*, 1920, **32**, 99) are in the main confirmed and explained by our findings.

The experiments with cellulose gave, in quantitative respects, results very similar to those with sugar. The coke yields in the first and second groups are slightly higher, which may be due to the somewhat higher carbon content of the cellulose molecule. A noteworthy distinction lies in the discrepancy between the wet and dry method with these two substances. The sugar gives a higher yield by the wet method in thirty-one, and cellulose in only twelve, out of forty-one cases. The tendency is therefore for sugar to give a higher result by wet carbonising and for cellulose by dry carbonising.

Another distinction between the two substances lies in the velocity of carbonisation. A rough measurement of this was obtained by noting the time when the flame at the crucible lid disappeared.

The following are averages from all the tests :

| | Wet method. Flame disappears after | Dry method. | |
|---|---|---|---|
| Sugar ..... | 41 | 29 | seconds |
| Cellulose ..... | 131 | 77 | „ |

The difference between the " wet " and " dry " values may be taken as the time required for driving off water. The much slower rate of carbonisation of cellulose is due in part to the less efficient transference of heat into the paper plug as compared with the fused sugar covering the crucible bottom, but must be partly accounted for by the constitutional differences of the two carbohydrates.

The effect of catalysts on the coke yield obtained has a bearing on the question of charcoal activation, the implication being that the density, size, and shape of pores and the true and apparent density of the char are subject to similarly great variation. This view is supported by the work of Firth and Watson (*Trans. Faraday Soc.*, 1924, **19**, 601), who found that charcoal prepared from sugar, to which iron had been added before carbonisation, had its activity for the catalytic decomposition of hydrogen peroxide considerably increased.

*Experiments with Coal.*

A few preliminary experiments were made with coal, although the disadvantage of its inherent ash was realised. In order to reduce this to a minimum, the constituents having the smallest percentage of mineral matter were selected and, moreover, the acid-soluble mineral constituents were extracted with hydrochloric acid.

Dalton Main (S. Yorks) coking coal was used. After grinding to pass through a 10-mesh sieve, the fusain and some fine dust were removed by elutriation. The remainder, after screening into portions larger and smaller than 30 mesh, was subjected to float-and-sink tests, according to the method described by one of us (*Trans. Inst. Min. Eng.*, 1921, **60**, 288). The fraction $D < 1{\cdot}35$ passing through 30-mesh, which consisted mainly of clarain and some vitrain, was used in the following tests. It contained originally 1·11% of ash; by extraction with hydrochloric acid and washing, this was reduced to 0·86% of the following composition :

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $K_2O$ |
|---|---|---|---|---|
| 0·43 | 0·29 | 0·04 | 0·09 | 0·01% |

It consisted therefore principally of clay or shale.

The impregnation of the coal was done with solutions of the same concentration and in the same proportion as in the case of sugar and cellulose. Carbonisation was only carried out by the

dry method. According to the reagent used, its solution was either dried in admixture with the coal, or else it was precipitated on the coal, or, in the case of insoluble or sparingly soluble compounds, mixed with it dry or in suspension with subsequent drying. It was found that care had to be exercised in obtaining homogeneous mixtures, as in precipitating ferric hydroxide, for instance, a tendency was noticed to impregnate the smaller particles and leave the larger ones uncoated.

Since there was no difficulty in carbonising this coal in the electric coking furnace, as had been experienced in the case of sugar, this was done and the yields of coke, tar, and gas were determined. The tests were carried out as specified in the Interim Report on Coal Analysis of the Fuel Research Board, 1923; coking time 7 minutes.

The coherent coke cylinders and the loose, small flakes of retort carbon, forming together the solid carbonised residue, were weighed separately. The results are recorded in Table IV, being arranged in order of the coke yield after deducting therefrom the added catalyst or the compound formed from it.

The reason for recording retort carbon separately from coke is that the former must be regarded as representing a primary decomposition product, originally volatile, but subsequently subjected to secondary thermal decomposition. The coke yield decreases as the formation of retort carbon increases. The influence of the catalyst is, however, not restricted to the variation between coke and retort carbon, for it will be seen that the combined values of these two products still show very considerable differences according to the compound added. The tar roughly increases as the coke decreases. The percentage variation is considerably greater than that of the coke.

Inasmuch as the retort carbon might be regarded as representing volatile liquids, in which form it is actually obtained in low-temperature carbonisation, a column for the combined values of tar and retort carbon was added, which shows the most remarkable range of differences, the highest value being just double that for the untreated coal.

The rate of gas-making was observed in half-minute readings, the curves being very close together. It remained therefore unaffected by the addition of the various catalysts, as does the final yield of gas; the discrepancies shown in the table are practically within the experimental error.

The results show that the effect of the catalysts is a distribution between the solid and liquid products of coal carbonisation, the gas yield being merely a function of the temperature of carbonisation.

## TABLE IV.

*Influence of Catalysts on the Carbonisation of Coal at* 900°.

Clarain and Vitrain ($D<1{\cdot}35$) from Dalton Main.

Through 30-mesh sieve. HCl-extracted.

| | Coke less compd. formed. %. | Retort carbon. %. | Tar. %. | Gas (c.c. per gm.). | Coke + retort carbon. %. | Tar + retort carbon. %. |
|---|---|---|---|---|---|---|
| $FeCl_3$ | 65·72 | 1·32 | 17·59 | 254 | 67·04 | 18·91 |
| $H_2SO_4$ | 64·33 | 1·07 | 18·15 | 262 | 65·40 | 19·22 |
| $FeSO_4$ | 64·04 | 1·94 | 20·85 | 256 | 65·98 | 22·79 |
| $Na_2SiO_3$ | 63·69 | 1·09 | 20·12 | 249 | 64·78 | 21·21 |
| $Na_2CO_3$ | 63·50 | 1·74 | 20·37 | 245 | 65·24 | 22·11 |
| $SiO_2$ | 63·34 | 1·51 | 21·28 | 252 | 64·85 | 22·79 |
| $Al_2O_3$ | 62·92 | 1·95 | 22·13 | 243 | 64·87 | 24·08 |
| $K_2CO_3$ | 62·77 | 1·41 | 21·69 | 244 | 64·18 | 23·10 |
| 2NaCl | 62·28 | 1·82 | 20·76 | 255 | 64·10 | 22·58 |
| $\frac{1}{2}Fe_2O_3$ | 62·23 | 3·34 | 24·05 | 245 | 65·57 | 27·39 |
| CaO | 61·08 | 3·42 | 20·20 | 253 | 64·50 | 23·62 |
| MgO | 60·94 | 3·57 | 22·05 | 248 | 64·51 | 25·62 |
| $(COONa)_2$ | 59·92 | 3·69 | 19·73 | 258 | 63·61 | 23·42 |
| $Na_2SO_4$ | 57·62 | 5·34 | 26·17 | 269 | 62·96 | 31·51 |
| Untreated | 53·68 | 8·48 | 29·02 | 255 | 62·16 | 37·50 |

The number of catalysts tried so far is considerably smaller than that used in the sugar and cellulose experiments. They arrange themselves, however, in practically the same order, with the untreated coal at the bottom of the list. It is somewhat surprising that the external appearance and size of the coke cylinders obtained do not vary to any extent, but there are indications that their internal structure, and consequently the density, porosity, and reactivity differ very considerably, as indeed is implied by the combination of varying weight and constant volume.

It should be remembered that the coal examined consists only of clarain and vitrain. As one of us pointed out (J., 1920, **117**, 253), the formation and susceptibility to "cracking" of the primary liquid products from clarain, vitrain, and durain respectively, indicate a considerable difference in their chemical nature. The results obtained must therefore not be applied without discrimination to other coal constituents, and still less to coals of different type or origin.

They are, however, sufficiently definite to show that a great deal, if not the bulk, of the research work which has been done on the carbonisation of coal and other fuels is subject to considerable revision, as in most of this work the influence of the composition of the mineral matter, apart from the amount, on the course of the carbonisation of coal was entirely neglected.

We desire to express our best thanks to the Fuel Research Board, Department of Scientific and Industrial Research, which enabled one of us (M. A. L. B.) to devote his time to this research. We are also indebted to Mr. A. H. Raine, who carried out some preliminary experiments on the subject.

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317, HIGH HOLBORN, W.C. 1. [*Received, July 30th*, 1924.]

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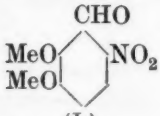
## CCCXVII.—*Nitration of* 2 : 3-*Dimethoxybenzaldehyde.*

By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and FRANCIS WILBERT STOYLE.

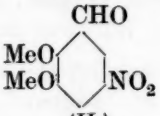
IN the course of experiments on the synthesis of ψ-opianic acid, considerable quantities of 6-nitro-2 : 3-dimethoxybenzaldehyde were required and the preparation of this substance was attempted by the method of Perkin, Roberts, and Robinson (J., 1914, **105**, 2389). As stated by these authors (compare also Davies, J., 1923, **123**, 1584), the product of the nitration of *o*-veratraldehyde has the composition of a mononitro-derivative, exhibits the constant melting point, 88°, not altered by recrystallisation, and yields an indigotin when treated with acetone and aqueous sodium hydroxide. Moreover, the acid obtained on oxidation also appeared to be homogeneous. It was therefore surprising to find that this mononitro-*o*-veratraldehyde, m. p. 88°, when condensed with *p*-toluidine, yielded two isomeric * substances, separable by crystallisation from alcohol, and melting at 143° and 104°. The nature of these substances and the heterogeneity of the product, m. p. 88°, was proved by the hydrolysis of the Schiff bases, which yielded the isomeric nitro-*o*-veratraldehydes, m. p's. 115° and 110°, respectively. The latter is 6-nitro-2 : 3-dimethoxybenzaldehyde (I), because it may be converted into the tetramethoxyindigotin described by Perkin, Roberts, and Robinson (*loc. cit.*), whilst the former is identical with 5-nitro-2 : 3-dimethoxybenzaldehyde (II), already prepared by Davies (*loc. cit.*) by methylation of the product of nitration of *o*-vanillin. On oxidation, this aldehyde yields 5-nitro-2 : 3-dimethoxybenzoic acid, m. p. 176°, as recorded by Cain and Simonsen (J., 1914, **105**, 159) for the product of nitration of *o*-veratric acid, which was proved

* At first, it occurred to us that the *o*-veratraldehyde might have been incompletely nitrated, but 2 : 3-*dimethoxybenzylidene*-p-*toluidine* crystallises from alcohol in colourless, glistening prisms, m. p. 93°. It may also be mentioned that 6-*nitro*-3 : 4-*dimethoxybenzylidene*-p-*toluidine* crystallises from alcohol in yellow needles, m. p. 133°. In both cases, only one substance was isolated from the reaction.

to be a *m*-nitrobenzoic acid. A freezing-point diagram of mixtures of 5- and 6-nitro-*o*-veratraldehydes has been constructed, and examination of the nitration product by its aid indicates the presence of a third substance in the mixture. Roughly, however, the aldehydes were found to be present in equal proportions, and equal quantities of the two isomerides, when crystallised together from alcohol, separate in apparently homogeneous needles, m. p. 88°. It still remains a remarkable fact that a considerable proportion of 6-nitro-*o*-veratraldehyde should be formed in the nitration of *o*-veratraldehyde, because, whilst the two methoxy-groups should affect positions 5 and 6 equally, the aldehydo-group might be



(I.)



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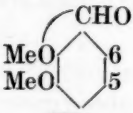


(III.)

expected to induce preferential substitution in position 5. On quite general grounds, it is not difficult to correlate the phenomenon with well-recognised effects of substituents in the benzene nucleus on each other. (1) It appears to be a general rule that the introduction of *m*-directive groups reduces the ease of further substitution by such groups. (2) Where the reactivity of the nucleus is enhanced, for example, by direct union with nitrogen or oxygen, the *m*-directive groups have a greater depressing effect on the ease of further substitution if they are situated in the positions in which they can be introduced by direct substitution. There are many examples of the application of this rule, but one may suffice for purposes of illustration. *m*-Nitrophenol and *p*-nitrophenol are, according to (1), less nuclear-reactive than phenol, and that is, of course, the case. In harmony with the rule now formulated, *m*-nitrophenol should exhibit greater nuclear-reactivity than the *p*-isomeride. This is again in accordance with experience, since further substitutions are much more readily accomplished in the case of the meta-isomeride.

Now, in *o*-veratraldehyde (III), the aldehydo-group is a *m*-directive group situated in the *o*-position to a methoxyl and in the *m*-position to a second methoxyl, and according to the above rules it should depress the reactivity of the *o*-methoxyl to the greater extent and thus favour substitution in position 6. That the effect is not so overwhelming as previously supposed, is probably due to the influence of steric hindrance and also to the circumstance that –CHO is a weak *m*-directive group. It is curious that the type of effect here considered is not exerted to a great extent by the carboxyl group, and the ease with which salicylic acid couples with

the diazonium salts is thus correlated with the production of 5-nitro-*o*-veratric acid by nitration of *o*-veratric acid (Cain and Simonsen, *loc. cit.*).

## EXPERIMENTAL.

*The Nitro-2 : 3-dimethoxybenzylidene-p-toluidines.*—The nitration of *o*-veratraldehyde was carried out essentially as described by Perkin, Roberts, and Robinson (*loc. cit.*); the product, m. p. 88°, appeared to be a homogeneous substance and suffered no change on repeated fractional crystallisation from benzene–ligroin. This material (21·1 g.) was heated with *p*-toluidine (10·7 g.) during 10 minutes on the steam-bath, water separating. Alcohol (250 c.c.) was then added and the mixture heated until complete solution occurred. On cooling, *5-nitro-2 : 3-dimethoxybenzylidene-p-toluidine* separated first, and then the 6-nitro-derivative. These substances can be completely purified by careful fractional crystallisation from alcohol. 5-Nitro-2 : 3-dimethoxybenzylidene-*p*-toluidine occurs in slender, colourless needles, m. p. 143° (Found : C = 64·0; H = 5·3; N = 9·1. $C_{16}H_{17}O_4N_2$ requires C = 63·8; H = 5·3; N = 9·3%). This substance was isolated in an amount corresponding to 53% of the total nitro-*o*-veratrylidene-*p*-toluidines obtained.

*6-Nitro-2 : 3-dimethoxybenzylidene-p-toluidine* is more readily soluble in alcohol than its isomeride and separates from moderately concentrated solutions in colourless, glistening, rhombic plates, m. p. 104° (Found : C = 64·2; H = 5·5; N = 9·4%).

*The Nitro-2 : 3-dimethoxybenzylideneanilines.*—The preparation of these substances was carried out in a manner closely similar to that employed in the case of the *p*-toluidine derivatives. The isomerides were again separated by fractional crystallisation from alcohol. *5-Nitro-2 : 3-dimethoxybenzylideneaniline* is the more sparingly soluble and separates from alcohol in fine, colourless needles, m. p. 122° (Found : N = 9·8. $C_{15}H_{15}O_4N_2$ requires N = 9·8%). The amount of this isomeride isolated amounted to 47% of the mixture. The *hydrochloride* separates when hydrogen chloride is passed into an ethereal solution of the base. On heating, it turns red at about 180° and melts at 200°.

*6-Nitro-2 : 3-dimethoxybenzylideneaniline* crystallises in short, colourless needles, m. p. 84° (Found : N = 9·9%). The *hydrochloride* melts at 156° with decomposition.

*5-Nitro-2 : 3-dimethoxybenzaldehyde* (II) was readily obtained from the pure *p*-toluidine or aniline derivatives, m. p's. 143° and 122°, respectively, by hydrolysis with hot dilute hydrochloric acid. It crystallises from benzene–light petroleum (b. p. 80—100°) in long, colourless needles, m. p. 115° (Found : N = 6·6. $C_9H_9O_5N$ requires N = 6·6%). On oxidation with a warm alkaline solution of potass-

ium permanganate, this aldehyde yields 5-nitro-2 : 3-dimethoxybenzoic acid, m. p. 176°. It cannot be converted into an indigotin derivative by treatment with acetone and aqueous sodium hydroxide. The *dimethyl acetal* was prepared by boiling under reflux for ½ hour a solution of the aldehyde in methyl alcohol (6 parts), to which two or three drops of nitric acid had been added. On cooling, the derivative separated in small, colourless prisms, m. p. 89° (Found: N = 5·2. $C_{11}H_{15}O_6N$ requires N = 5·4%). The *phenylhydrazone* crystallised from much alcohol in bright red, hexagonal plates, m. p. 179°, the *semicarbazone* from aqueous alcohol in colourless, woolly needles, m. p. 210°, and the *oxime* from alcohol in slender needles, m. p. 155°.

6-*Nitro*-2 : 3-*dimethoxybenzaldehyde* (I).—Hydrolysis of the nitro-*o*-veratrylidene-*p*-toluidine, m. p. 104°, or the corresponding aniline derivative, m. p. 84°, by means of hot dilute hydrochloric acid yields the aldehyde, which crystallises from benzene–ligroin (b. p. 80—100°) in slender, colourless needles, m. p. 110° (Found: N = 6·6. $C_9H_9O_5N$ requires N = 6·6%). The derivatives of this aldehyde are very much more readily soluble in alcohol than those just described. On treatment with acetone and aqueous sodium hydroxide, tetramethoxyindigotin was readily obtained. The *dimethyl acetal* crystallises slowly from methyl alcohol in colourless cubes, m. p. 72°, which turn green on exposure to light and air.

The *phenylhydrazone* crystallised from alcohol in brown-orange prisms, m. p. 138°, the *semicarbazone* from aqueous alcohol in short needles, m. p. 227—228°, and the *oxime* from aqueous alcohol in needles, m. p. 130°.

6-Nitro-2 : 3-dimethoxybenzoic acid crystallises from water in colourless, glistening, flat prisms, m. p. 183°. The melting point at 179° recorded by Perkin, Roberts, and Robinson (*loc. cit.*) is that of a mixture with 5-nitro-2 : 3-dimethoxybenzoic acid.

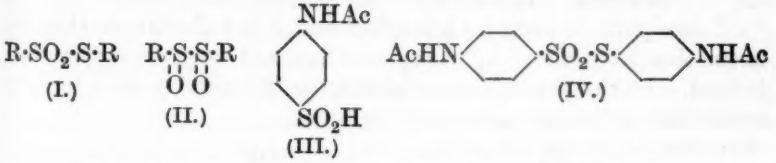
One of the authors (F. W. S.) desires to express his gratitude to the Advisory Council of the Department of Scientific and Industrial Research for grants which have enabled him to take part in this investigation.

UNIVERSITIES OF OXFORD AND
MANCHESTER. [*Received, August 12th*, 1924.]

# CCCXVIII.—*Derivatives of Aniline Disulphoxide.*

By Charles Montague Bere and Samuel Smiles.

In a recent discussion of the structure of aromatic disulphoxides (this vol., p. 176), it was concluded that the symmetrical structure which is commonly assigned to these substances is by no means fully justified, whilst the unsymmetrical thiosulphonate arrangement (I) not only accords with the facts but has important advantages. Previous workers on this subject have considered the suggestion (Hilditch, J., 1910, **97**, 1098; Hinsberg, *Ber.*, 1908, **41**, 2836; Fries, *Ber.*, 1914, **47**, 1195) that this structure might undergo intramolecular change to the symmetrical arrangement (II). No definite evidence of this change has been adduced, but the record of two isomeric forms of acetanilide-*p*-disulphoxide is interesting from this point of view and warranted the further study of the substance. The isomerides in question were obtained by Hinsberg (*Ber.*, 1909, **42**, 1278) from a material formed by the action of hydrogen peroxide on α-acetanilide *p*-disulphoxide (m. p. 215°). This oxidation product was of doubtful character, but it appeared to be a compound of the sulphide and disulphoxide in equimolecular proportions. Brief extraction of this material with boiling acetic acid gave the "α"-disulphoxide, whilst prolonged treatment gave the "β"-compound. The distinction between the two substances is not at all clear; both are described as yellow material, the "α"-isomeride as retaining two molecules of acetic acid and melting at 190°, and the "β" as capable of retaining the same proportion of solvent, but the melting point is quoted (233°) for a sample free from it. This indirect method of preparing the substance by the decomposition of a material of doubtful character seemed hardly satisfactory, hence in the present experiments the common method of obtaining disulphoxides was adopted. Acetanilide-*p*-sulphonyl chloride was




converted by the usual method to the sulphinic acid (III) and this, when treated with very dilute hydrogen iodide in presence of sulphurous acid, yielded acetanilide *p*-disulphoxide (IV). When freshly prepared, this substance is colourless, but on exposure to light it becomes bright yellow without change in melting point (235°) or composition. The colour slowly fades when a sample is

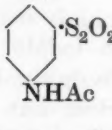
kept in the dark and it is removed when the substance is crystallised from acetic acid. After separating from the warm solvent, the substance retains acetic acid, but apparently not in any definite molecular proportion; in this condition, the colourless and coloured materials melt and decompose at about 218—219°. The substance is evidently phototropic; a comparison of its properties with those of Hinsberg's " β "-compound leaves little doubt as to the identity of the two. The latter is described as melting at 233° when free from acetic acid and as being obtained in the colourless state when crystallised from that solvent.

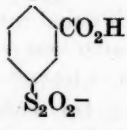
The constitution of the substance now described is established by the reduction to acetanilide *p*-disulphide (VI) and by the reaction with acetanilide *p*-mercaptan which yields acetanilide-*p*-sulphinic acid and the same disulphide (V) :

$$\begin{matrix} AcHN\cdot C_6H_4\cdot SO_2\cdot S\cdot C_6H_4\cdot NHAc \\ HS\cdot C_6H_4\cdot NHAc \end{matrix} \qquad (AcNH\cdot C_6H_4\cdot S-)_2$$

(V.) (VI.)

It is interesting to notice that in both reactions the β-disulphide (m. p. 182°) is formed. Hinsberg obtained the α-disulphide (m. p. 215°) by reducing the disulphoxide, but this different result is explained by the fact that his laboratory was infected with the α-sulphide, and all attempts to obtain the β-compound at the time by other methods failed (Hinsberg, *loc. cit.*, p. 1280, footnote). The stability relations of these disulphides are at present obscure; during the experiments now described, the conversion of the β- to the α-compound could not be effected, and a similar experience has been recorded by Zincke and Jörg (*Ber.*, 1909, **42**, 3374). This failure to obtain the disulphide precluded any attempt to prepare the " α "-disulphoxide by Hinsberg's method, but it may be mentioned that the formation of the intermediate compound by combination of the β-disulphide with the phototropic disulphoxide could not be realised. Hence for the present the nature of the " α "-disulphoxide remains uncertain and it is unfortunate that the distinction from the " β "-compound has not been more precisely defined. In the present experiments, no distinct isomeric form of acetanilide *p*-disulphoxide could be found.

(VII.) 

(VIII.)

Since phototropy of disulphoxides has not been previously observed, other derivatives of this group have been examined.

Aniline *p*-disulphoxide was obtained as a yellow, crystalline material; on the other hand, benzanilide *p*-disulphoxide is colourless and is very slowly altered by exposure to light. Moreover, the meta-position of the acetylamino-group is not favourable to the phenomenon, since 4 : 4′-diacetylaminoditolyl 2 : 2′-disulphoxide (VII) is colourless and unaffected by light. A similar stability was observed with the derivative of salicylic acid (VIII) containing hydroxyl in the para-position to the disulphoxide group. Further investigation of the phototropic properties of disulphoxides is being made.

## Experimental.

*Acetanilide*-p-*sulphinic Acid* (III).—Acetanilide-*p*-sulphonyl chloride (Stewart, J., 1922, **121**, 2558) was shaken (20 g.) with a weakly alkaline solution of sodium sulphite (60 g. in 200 c.c.), and the *sulphinic acid*, liberated (yield 70%) by the cautious addition of sulphuric acid to the filtered solution, was crystallised from hot water, being obtained in colourless needles, m. p. 180° (decomp.) (Found: N = 7·3; S = 16·4. $C_8H_9O_3NS$ requires N = 7·0; S = 16·1%).

*Acetanilide* p-*Disulphoxide* (IV).—An aqueous solution of the sulphinic acid (10 g. in 250 c.c.) containing a few drops of hydriodic acid and an excess of sulphurous acid was heated for about ½ hour on the water-bath, cooled, and neutralised with sodium carbonate. The *disulphoxide*, which remained as a colourless, insoluble material (yield 90%), crystallised from hot acetic acid in colourless needles, m. p. about 219° (decomp.), retaining varying quantities of acetic acid which was lost at 130°; the m. p. was now 235° (decomp.) (Found: C = 52·6; H = 4·4; N = 7·6. $C_{16}H_{16}O_4N_2S_2$ requires C = 52·7; H = 4·4; N = 7·7%).

The disulphoxide was reduced by heating a concentrated solution in acetic acid for 2 hours at 100° with hydrogen iodide and excess of sulphurous acid. The product, isolated by addition of water, was β-acetanilide *p*-disulphide (m. p. 183°). The conversion of this substance to the α-isomeride could not be realised (Found: N = 8·7. $C_{16}H_{16}O_2N_2S_2$ requires N = 8·5%). A solution of equimolecular proportions of acetanilide *p*-disulphoxide and acetanilide *p*-mercaptan (Zincke and Jörg, *Ber.*, 1909, **42**, 3367) in alcohol was heated for 1 hour on the water-bath, and excess of sodium carbonate added, the disulphide being precipitated. The solution was concentrated, and acidified with sulphuric acid, when acetanilide-*p*-sulphinic acid was liberated and identified in the usual manner.

Whether free from acetic acid or containing it, this substance became bright yellow on exposure to light, but this colour was slowly lost when a sample was kept in the dark for some months.

*Aniline* p-*Disulphoxide*, $(NH_2 \cdot C_6H_4)_2S_2O_2$.—A solution of acetanilide *p*-disulphoxide in concentrated hydrochloric acid was boiled for ½ hour, cooled, and treated with an excess of dilute aqueous sodium carbonate; the *disulphoxide*, which separated (80% yield) as crystalline material, was obtained from aqueous alcohol in bright yellow needles, m. p. 175° (decomp.). The colour was deepened by exposure to light (Found: N = 9·9; S = 23·0. $C_{12}H_{12}O_2N_2S_2$ requires N = 10·0; S = 22·9%).

4 : 4′-*Diacetylaminoditolyl* 2 : 2′-*Disulphoxide* (VII).—A suspension of 4-acetylaminotoluene-2-sulphinic acid (J., 1923, **123**, 2385) (16 g.) in water (400 c.c.) containing a few drops of hydrogen iodide and an excess of sulphurous acid was heated on the water-bath for 2 hours; the *disulphoxide* (yield 90%), isolated in the usual manner, crystallised from aqueous alcohol in colourless prisms, m. p. 180° (decomp.) (Found: N = 6·8; S = 16·4. $C_{18}H_{20}O_4N_2S_2$ requires N = 7·1; S = 16·35%). When reduced by hydrogen iodide in acetic acid, it gave 4 : 4′-diacetylaminoditolyl 2 : 2′-disulphide (m. p. 224°; Zincke, *Ber.*, 1912, **45**, 1502). Attempts to obtain the disulphoxide from 3-acetylamino-*p*-xylene-6-sulphinic acid yielded the corresponding disulphide (J., 1923, **123**, 2387). The same method readily converted 5-sulphinosalicylic acid (Stewart, *loc. cit.*) to

*Salicylic Acid* 5-*Disulphoxide* (VIII).—This substance (yield 60%) separated from aqueous acetone in colourless needles, m. p. 206—208° (decomp.) (Found: C = 45·5; H = 2·9; S = 17·1. $C_{14}H_{10}O_8S_2$ requires C = 45·4; H = 2·7; S = 17·3%).

*Benzanilide*-p-*sulphonyl chloride*, $NHBz \cdot C_6H_4 \cdot SO_2Cl$, was most readily obtained by keeping a solution of benzanilide (10 g.) in chlorosulphonic acid (16 c.c.) at 60° for 1 hour, and pouring the mixture over ice (yield 90%). After purification from acetone and water, the substance, m. p. 180°, was identified with a sample prepared by the method of Schroeter (*Ber.*, 1906, **39**, 1565), in which benzoylsulphanilic acid was treated with phosphorus pentachloride.

*Benzanilide*-p-*sulphinic acid*, $NHBz \cdot C_6H_4 \cdot SO_2H$, prepared by constantly shaking a mixture of the sulphonyl chloride (10 g.) with an aqueous solution of sodium sulphite (30 g. in 200 c.c.), and isolated from the alkaline liquid in the usual manner (yield 70%), crystallised from acetone in colourless needles, m. p. 206° (decomp.), insoluble in water (Found: C = 59·5; H = 4·7; S = 12·4. $C_{13}H_{11}O_3NS$ requires C = 59·7; H = 4·3; S = 12·3%).

The conversion of this substance to *benzanilide* p-*disulphoxide* was carried out in alcoholic solution with the usual reagents. The substance was insoluble in ordinary volatile solvents and was slightly

soluble in some of high boiling point, but on recrystallisation from the latter decomposition took place; hence the substance could not be obtained in a pure condition. The various samples isolated decomposed at about 220° and on exposure to light slowly assumed a yellow colour.

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, September 10th*, 1924.]

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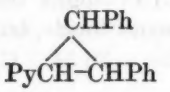
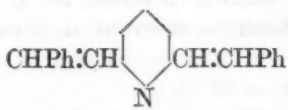
## CCCXIX.—2 : 6-*Distyrylpyridine and its Derivatives.*

By BRIAN DUNCAN SHAW.

THE base melting at 164° obtained by Ladenburg as a by-product in the preparation of 2-stilbazole from α-picoline and benzaldehyde (*Ber.*, 1903, **36**, 118), which he regarded as diphenylpyridyl*cyclo*propane (I), is now shown to be 2 : 6-distyrylpyridine (II).

(I.)  (II.) 

It is produced from the 2 : 6-lutidine which is present in ordinary α-picoline. Ladenburg's error is somewhat singular, since "dibenzylidene-lutidine" had already been prepared by Schuster (*Ber.*, 1892, **25**, 2403), while working under Ladenburg at Breslau. The mode of formation and the properties of the base studied by the author leave no doubt as to its identity with the compounds obtained by Ladenburg and by Schuster. It was shown to be 2 : 6-distyrylpyridine by analysis, by its reactions, and by direct comparison with an authentic specimen prepared from 2 : 6-lutidine. Schuster's results (*loc. cit.*) have been confirmed except in the case of the tetrabromide. By following the directions given by him, the dibromide only is obtained, a compound which Schuster does not mention. Moreover, the tetrabromide prepared by the author agrees in no respect with that described by Schuster.

### EXPERIMENTAL.

2 : 6-*Distyrylpyridine* was separated from the crude product of the action of benzaldehyde on impure α-picoline, by means of its sparingly soluble hydrochloride (this vol., p. 1932), which was freed from tar by extraction with benzene, recrystallised from

alcohol (golden-yellow needles, m. p. 215° in a sealed tube; Ladenburg gives m. p. indefinite, not completely molten at 220°), and decomposed with hot pyridine; the base separated, on cooling, in snow-white needles, m. p. 164° (Ladenburg, m. p. 164°). A further quantity was obtained by diluting the pyridine mother-liquor with water, filtering, and washing the flocculent precipitate with alcohol. For analysis, the base was twice crystallised from benzene and dried at 100°; the melting point was unaltered (Found: C = 89·02; H = 6·0; N = 4·76. Calc., C = 89·04; H = 6·0; N = 4·95%). Its solution in benzene or alcohol showed the violet fluorescence noted by Ladenburg.

*Halogen Derivatives of* 2 : 6-*Distyrylpyridine.*—The base very slowly combines additively with bromine at the ordinary temperature; in warm carbon disulphide solution (the conditions under which Schuster claims to have prepared the tetrabromide), a dibromide is produced. This is best prepared by adding bromine (1·26 g. in carbon disulphide) to the base (2 g. in boiling carbon disulphide, 20 c.c.); the yellow precipitate is washed with alcohol and recrystallised from benzene–chloroform. 2 : 6-*Distyrylpyridine dibromide*, minute needles, m. p. 214—215° (slight decomp.), is soluble in benzene, chloroform, or carbon tetrachloride, but insoluble in alcohol or light petroleum (Found: Br = 36·34. $C_{21}H_{17}NBr_2$ requires Br = 36·12%).

2 : 6-*Distyrylpyridine tetrabromide*, prepared by boiling the base with excess of bromine in carbon tetrachloride solution for several hours, separated from the solution, on cooling, in well-defined, rhombic prisms, soluble in carbon tetrachloride or chloroform, insoluble in alcohol, m. p. 179° (with evolution of hydrogen bromide) (Found: Br = 52·8. Calc., Br = 53·08%). Schuster states that this compound crystallises from alcohol in needles, m. p. 183°.

2 : 6-*Distyrylpyridine dichloride*, prepared by the action of chlorine on the base in carbon tetrachloride solution, and recrystallised from this solvent, formed minute needles, m. p. 213°, insoluble in alcohol (Found: Cl = 20·20. $C_{21}H_{17}NCl_2$ requires Cl = 20·07%).

*Reduction of* 2 : 6-*Distyrylpyridine.*—The base (10 g. in boiling absolute amyl alcohol, 250 c.c.) was reduced with a large excess of sodium until the metal ceased to react, water was then added, the mixture well shaken, and the amyl-alcoholic layer, containing the partly reduced base, washed with water and dried by distillation. The reduction was repeated to effect complete hydrogenation. The mixture was diluted with water and acidified, the amyl alcohol removed with steam, and excess of caustic soda added to the residual solution. The new base, liberated as an oil, was converted into the hydrochloride, which was, after recrystallisation, decom-

posed with alkali, and the base distilled under diminished pressure. 2 : 6-*Di*-β-*phenylethylpiperidine* is a colourless oil, b. p. 290—295°/20 mm., which becomes viscous, but does not crystallise when cooled in a freezing mixture (Found : C = 86·1; H = 9·25. $C_{21}H_{27}N$ requires C = 86·0; H = 9·22%). The salts are colourless, in contradistinction to those of 2 : 6-distyrylpyridine. The *oxalate* crystallises from dilute alcohol in clusters of fine needles, m. p. 179° (Found : in salt dried at 100°, C = 72·2; H = 7·6; N = 3·5. $C_{21}H_{27}N,C_2H_2O_4$ requires C = 72·1; H = 7·6; N = 3·6%). The *hydrochloride*, aggregates of needles, m. p. 183°, from dilute alcohol, is sparingly soluble in water (Found : Cl = 10·57. $C_{21}H_{27}N,HCl$ requires Cl = 10·79%). The *nitrate*, plates, m. p. 167—170° (decomp.), from dilute alcohol, is sparingly soluble in water.

The author wishes to express his thanks to Professor F. S. Kipping, F.R.S., for his kind interest in this research, and to the Department of Scientific and Industrial Research for a maintenance grant which has enabled the work to be carried out. He is indebted to the South Metropolitan Gas Company for gifts of pure α-picoline and crude pyridine.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 20th*, 1924.]

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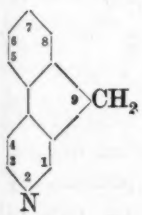
## CCCXX.—*Pyridofluorene and some of its Derivatives.*

By WILLIAM HOBSON MILLS, WILLIAM HAROLD PALMER, and MARGARET G. TOMKINSON.

THE preparation and examination of pyridofluorene (I) and some of its derivatives was undertaken in the hope of discovering facts which would throw light on the isomerism occurring among certain of the 9-derivatives of fluorene (Schmidt and Mezger, *Ber.*, 1906, **39**, 3895; Schmidt and Stützel, *ibid.*, 1908, **41**, 1243), of which no satisfactory explanation has been given.



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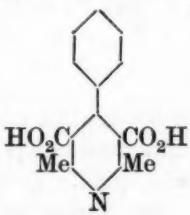

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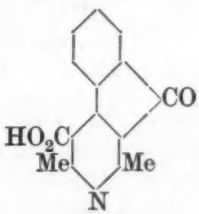

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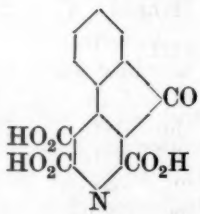
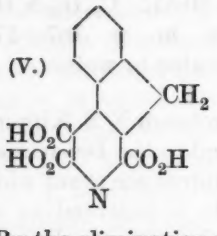
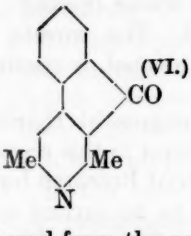


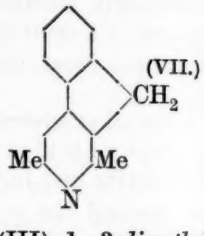
(IV.)

Although this object was not attained, a description of the new compounds prepared may be of use. Starting with phenyl-lutidine-

dicarboxylic acid (II), which is easily prepared from benzaldehyde, ethyl acetoacetate, and ammonia (Schiff and Puliti, *Ber.*, 1883, **16**, 1607; Hantzsch, *ibid.*, 1884, **17**, 1512; Kirchner, *ibid.*, 1892, **25**, 2786), we obtained, by dehydration with concentrated sulphuric acid, 1 : 3-*dimethylpyridofluorenone*-4-*carboxylic acid* (III), which can be oxidised with potassium permanganate to *pyridofluorenone*-1 : 3 : 4-*tricarboxylic acid* (IV). Reduction of this with hydriodic acid and red phosphorus gives *pyridofluorene*-1 : 3 : 4-*tricarboxylic acid* (V) and this can be converted, best by heating its calcium salt with soda-lime, into the mother-substance of the series, *pyridofluorene* (I).



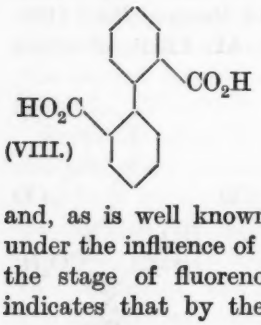



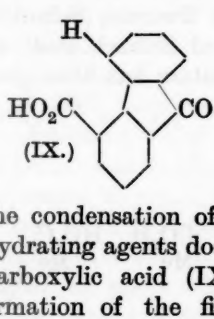



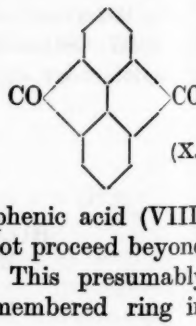

By the elimination of carboxyl from the acid (III), 1 : 3-*dimethylpyridofluorenone* (VI) was obtained and this was converted by reduction into 1 : 3-*dimethylpyridofluorene* (VII).

The isomeric 9-acetoxyfluorenes and 9-aminofluorenes appear to be stereoisomerides. If this is so, it would imply that the two hydrogen atoms in the 9-position differ from one another in their relation to the rest of the molecule, and this can only be if the three rings in the fluorene molecule are not coplanar.*

There is other evidence which tends to show that the fluorene molecule has not a plane configuration. We have found, for example, no indication that dimethylpyridofluorenonecarboxylic acid (III) could undergo further condensation to a compound of the type X,




and, as is well known, the condensation of diphenic acid (VIII) under the influence of dehydrating agents does not proceed beyond the stage of fluorenonecarboxylic acid (IX). This presumably indicates that by the formation of the five-membered ring in

* The explanation offered by Schmidt and his pupils (*loc. cit.*) assumes a different distribution of the valencies of the carbon atom from that generally accepted.

fluorenone the distance between the 5-carboxyl group and the 4-hydrogen atom is increased in the manner indicated in figure IX, for it is unlikely that the failure of the second carboxyl group to condense with the formation of the compound X is due to the increased resistance of the benzene nucleus to substitution owing to the presence of the carboxyl group in the *m*-position to the point of attack, seeing that in the somewhat similar formation of anthraquinone from benzoylbenzoic acid a second carbonyl group enters readily, even into the ortho-position to that already present. Moreover, if it is assumed that the configuration of the fluorene molecule can be roughly represented by a regular pentagon bearing regular hexagons on two of its sides, then, as is clear from Fig. 1, in the passage of a diphenyl- into a fluorenone-derivative a distortion of the kind suggested must ensue.*

FIG. 1.

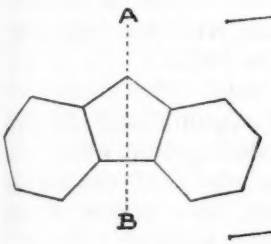



FIG. 2.

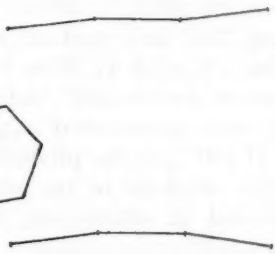


FIG. 3.

FIG. 4.

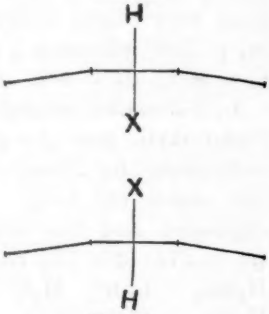



FIG. 5.




But if there is a lateral distortion of this kind of the bonds of the phenylene nuclei concerned in the formation of the five-membered ring, then the planes of the benzene rings must become inclined to that of the latter, either as indicated in Fig. 2, or in Fig. 3 (these are end-on views of the molecule along A B, Fig. 1), since by such inclination the strain consequent on this lateral distortion of the bonds would be partially relieved.

If the configuration of fluorene were that indicated by Fig. 3, the existence of its 9-derivatives in two modifications could be accounted for, since the substituent radical might lie either towards the convex or the concave side of the molecule, as in Fig. 4 or 5.

Since this configuration of the fluorene molecule (or indeed any other in which the 9-derivatives could occur in geometrically

* The stability of pyrene indicates that there would be no such difficulty in the corresponding formation of two six-membered rings, one on either side of the diphenyl molecule.

isomeric forms) would necessitate the molecular asymmetry of the unsymmetrically substituted derivatives, we have endeavoured to resolve fluorenonecarboxylic acid (IX) with alkaloids, and dimethylpyridofluorene (VI) and dimethylpyridofluorenone (V) with camphorsulphonic acids, but have obtained no evidence of the occurrence of resolution.

We do not, however, feel justified in drawing conclusions from these negative results.

## Experimental.

*4-Phenyl-lutidinedicarboxylic Acid.*—The diethyl ester of this acid (Schiff and Puliti, *loc. cit.*) was hydrolysed by boiling for 2 hours with an alcoholic solution of slightly more than the calculated quantity of sodium hydroxide (compare Kirchner, *loc. cit.*). From the aqueous solution of the resulting sodium salt the acid was precipitated by a slight excess of sulphuric acid. Recrystallised from very dilute hydrochloric acid, it formed colourless crystals, m. p. 296° (decomp.), not 280° as stated by Kirchner. (Found: C = 66·1; H = 4·9. Calc., C = 66·4; H = 4·8%).

*1 : 3-Dimethylpyridofluorene-4-carboxylic Acid.*—Phenyl-lutidinedicarboxylic acid (7·5 g.) and concentrated sulphuric acid (20 c.c.) were heated for 10 hours at 100°, and the product poured, when cool, into water (25 c.c.). The sulphate of the new acid was slowly deposited and was obtained in efflorescent, deep yellow prisms (m. p. 275—276°) by recrystallisation from 50% acetic acid (Found: $H_2SO_4$ = 15·8*; $H_2O$ = 15·4. $C_{15}H_{11}O_3N,\frac{1}{2}H_2SO_4,3H_2O$ requires $H_2SO_4$ = 16·2; $H_2O$ = 15·2%).

The acid was obtained by dissolving the sulphate in a slight excess of *N*-sodium hydroxide solution and adding *N*-hydrochloric acid until no further precipitation occurred: bright yellow crystals, m. p. 280·5° (decomp.), sparingly soluble in water or alcohol (Found: C = 71·2; H = 4·47. $C_{15}H_{11}O_3N$ requires C = 71·15; H = 4·35%). The potassium salt is sparingly soluble in cold water.

*Pyridofluorenone-1 : 3 : 4-tricarboxylic Acid.*—Dimethylpyridofluorenecarboxylic acid was dissolved in potassium hydroxide solution and heated at 60° with an aqueous solution of potassium permanganate (10% more than the theoretical quantity) until the latter was decolorised. To the filtrate from the manganese dioxide, after evaporation to small bulk and neutralisation with nitric acid, the calculated quantity of silver nitrate was added. The yellow silver salt thus precipitated was decomposed with the equivalent quantity of hydrochloric acid and the tribasic acid crystallised from the filtrate after concentration. It can be recrystallised by dis-

* On dried substance.

solving in hot water and precipitating with a few drops of hydrochloric acid: yellow plates, m. p. 203° (decomp.). Carefully heated, it resolidifies and the product melts again at 255°. It is sparingly soluble in ether or alcohol, readily in hot water, or aqueous alcohol (Found: C = 57·34; H = 2·37. $C_{15}H_7O_7N$ requires C = 57·53; H = 2·24%).

This compound can also be obtained, but less readily, by oxidising phenyl-lutidinedicarboxylic acid to phenylpyridinetetracarboxylic acid (Hantzsch, *Ber.*, 1884, **17**, 1515) and eliminating water from this with fuming sulphuric acid.

*Pyridofluorene*-1 : 3 : 4-*tricarboxylic Acid*.—Pyridofluorenonetricarboxylic acid (9 g.) was heated with hydriodic acid, b. p. 126° (90 c.c.) for 8 hours at 130°. The solution was then diluted with water, filtered, and most of the hydriodic acid removed by evaporation. On diluting the residue, the acid crystallised and was purified by dissolving in sodium carbonate solution and reprecipitating with hydrochloric acid and then crystallising from water; colourless needles, m. p. 255° (Found: C = 60·03; H = 3·16. $C_{15}H_9O_6N$ requires C = 60·20; H = 3·01%). A little more of the acid can be obtained by extracting the red phosphorus with sodium carbonate solution.

*Pyridofluorene*.—Calcium pyridofluorenetricarboxylate was mixed with soda-lime (8 parts) and distilled in a current of dry hydrogen at 40—50 mm. The product was a brown oil which slowly solidified. By recrystallisation from light petroleum (b. p. 40—50°) it was obtained as very pale yellow needles, m. p. 74·5° (Found: C = 86·06; H = 5·52. $C_{12}H_9N$ requires C = 86·22; H = 5·39%). The base was obtained in a purer form by distilling the acid itself in small quantities at a time (0·05 g.) and recrystallising the crystalline distillate from hot water: colourless needles, m. p. 78°.

1 : 3-*Dimethylpyridofluorenone*.—Dimethylpyridofluorenonecarboxylic acid was distilled in quantities of 2 g. and the reddish-brown, crystalline distillates were united and redistilled. The very pale yellow distillate recrystallised from light petroleum in almost colourless needles, m. p. 158° (Found: C = 80·1, 80·6; H = 5·4, 5·6; N = 6·5; *M* = 238, 220, 236. $C_{14}H_{11}ON$ requires C = 80·4; H = 5·3; N = 6·7%; *M* = 209).

Pyridofluorenetricarboxylic acid, distilled under diminished pressure, gave a compound crystallising from light petroleum in needles, m. p. 130°, which was presumably pyridofluorenone. It was not further investigated through lack of material.

1 : 3-*Dimethylpyridofluorene*.—Dimethylpyridofluorenone (1 g.) was heated with hydriodic acid, *D* 1·7 (10 c.c) and red phosphorus (2 g.) for 2 hours at the boiling point of the mixture. The spar-

ingly soluble hydriodide of the new base crystallised out and was extracted from the excess of phosphorus with hot water, from which it was deposited on cooling as bright yellow needles. The base was obtained from the hydriodide by decomposition with sodium carbonate; it formed colourless needles (from dilute alcohol), m. p. 87·5°. It dissolves sparingly in benzene, very sparingly in ether (Found: C = 85·91; H = 6·66. $C_{14}H_{13}N$ requires C = 86·15; H = 6·67%).

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[*Received, August 21st*, 1924.]

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# CCCXXI.—*Compounds of Tervalent Molybdenum. Part II. Molybdenyl Monochloride.*

By WILLIAM WARDLAW and ROBERT LOUIS WORMELL.

BY electrolytic reduction of molybdenum trioxide in hydrochloric acid of various concentrations, red or green solutions are obtained in which Chilesotti (*Z. Elektrochem.*, 1906, **12**, 173) has postulated the existence of isomeric chlorides similar to the green

$$[Cr4H_2O,Cl_2]Cl,2H_2O$$

and the violet $[Cr,6H_2O]Cl_3$, a conjecture supported by the recent work of Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458) on potential measurements of tervalent molybdenum solutions. Such isomerides have not yet been isolated from the reduced solutions, but by addition of alkali chlorides, complex salts of the types $[MoCl_6]R_3$ and $[MoCl_5,H_2O]R_2$ have been obtained. In attempting to isolate these isomeric chlorides, we succeeded in obtaining *molybdenyl chloride*, $MoOCl,xH_2O$, where $x$ is probably 4, from a highly concentrated solution containing tervalent molybdenum.

## EXPERIMENTAL.

*Molybdenyl Monochloride.*—A solution of molybdenum trioxide (60 g.) in 390 c.c. of hydrochloric acid (*d* 1·16) was heated on a water-bath for 8 hours, made up to 600 c.c., and electrolysed, in a diaphragm cell with smooth platinum electrodes (J., 1923, **123**, 969), until the cathode solution was olive-green. This solution was then concentrated at 50° under diminished pressure in an air-free flask; the colour changed from green to reddish-brown at *ca.* 250 c.c. After concentration to 180—200 c.c., the solution was transferred to a small cell and re-electrolysed. A solution was thus obtained having a much higher concentration of tervalent molybdenum than one prepared by direct dissolution of the tri-

oxide in concentrated hydrochloric acid. The electrolysis was continued till a sample of the cathode liquid, poured into acetone, gave an appreciable buff-coloured precipitate. The cathode solution was now forced by pressure of carbon dioxide into air-free acetone; the *oxychloride*, which separated as a heavy, buff-coloured powder in almost quantitative yield, was washed with acetone, alcohol, and dry ether, all these operations being performed in an atmosphere of carbon dioxide with rigid exclusion of air, and transferred to a desiccator filled with carbon dioxide, which was then evacuated.

*Valency of the Compound.*—A solution of the oxychloride in dilute sulphuric acid was titrated in an inert atmosphere with standard permanganate according to Reinhardt's method (Required: 48·03 c.c., 37·61 c.c.). A similar solution was oxidised with hydrogen peroxide, passed through the reductor (J., 1923, 123, 969), and titrated with the permanganate (Required: 48·1 c.c., 37·55 c.c.). The latter titrations represent the oxidation of tervalent molybdenum to the sexavalent state and it is evident that the molybdenum of the oxychloride is tervalent.

*Analysis.*—The molybdenum was precipitated as sulphide (Wardlaw, Nicholls, and Sylvester, this vol., p. 1911) and ignited. The chloride in the filtrate and washings was estimated as silver chloride (Found: Mo = 46·02, 45·99; Cl = 17·20, 17·16. Mo : Cl = 1 : 1·01; 1 : 1·01. $MoOCl,4H_2O$ requires Mo = 43·73. $MoOCl,3H_2O$ requires Mo = 47·64%). As the solid had been dried in an evacuated desiccator, it is probable that its normal hydrate is $MoOCl,4H_2O$.

*Properties and Reactions of Molybdenyl Monochloride.*—The dried solid is buff in colour, and does not deliquesce in the air, although its titration value gradually falls owing to air oxidation. It is readily soluble in water and in concentrated hydrochloric acid, yielding amber and reddish-brown solutions. It is insoluble in acetone or ether, but dissolves slightly in cold, readily in hot absolute alcohol. Cupric and mercuric chlorides are reduced to the "ous" condition, with further reduction to the metal by use of excess of the oxychloride. Ferric chloride also is readily reduced to the "ous" state. Sulphur, on boiling with a solution of the new solid, yields hydrogen sulphide. Sodium and ammonium hydroxides give black, flocculent precipitates, readily soluble in acids, which are probably the trihydroxides. Potassium cyanide reacts similarly. Potassium ferricyanide gives a deep red coloration. Silver nitrate is reduced to the metal, whilst lead acetate acidified with acetic acid gives no precipitate of lead chloride, indicating the absence of the chlorine ion.

*Conclusion.*

Tungsten and uranium do not yield analogues of molybdenyl monochloride, but vanadium, which should resemble it by reason of its diagonal position in the periodic table, forms a brown, insoluble oxychloride, VOCl. An oxychloride of chromium, $CrCl(OH)_2$, has been described, but the general method of preparation of tervalent chromium oxychlorides leads one to suspect that chance alone is responsible for the rational formulæ which have been ascribed to them (see Abegg, "Anorganische Chemie, IV, p. 98). Molybdenyl trichloride, $MoOCl_3$, is known only in the form of its complex salts $2RCl,MoOCl_3$, whilst the existence of the tetrachloride, $MoOCl_4$, is still doubtful. We are attempting to prepare these higher chlorides and are investigating the physicochemical properties of the monochloride. On the basis of the co-ordination theory, molybdenyl monochloride may be formulated thus, $\left[\begin{matrix}O\\ClMo4H_2O\end{matrix}\right]$, a representation which shows the usual co-ordination number, 6, of tervalent molybdenum and also signifies the non-precipitability of the chloride radical.

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## CCCXXII.—*The Density of the Oxides of Zirconium and Hafnium.*

By GEORGE HEVESY and VIGGO BERGLUND.

ALTHOUGH the amount of hafnium present in zirconium can be estimated by various chemical methods and by quantitative *X*-ray spectroscopy (Coster, *Chem. News*, 1923, **127**, 65), the analysis can be carried out much more easily and quickly by measuring the density of a mixture of the two oxides, for if the densities of both zirconium dioxide and hafnium dioxide are known the composition of the mixture can readily be calculated. Hafnium dioxide being nearly twice as dense as zirconium dioxide, this method is fairly sensitive and more trustworthy than several of those referred to above.

*The Density of Zirconium Oxide. General Considerations.*—Numerous determinations of the density of zirconium dioxide have given values varying between 5·45 and 5·89. Widely varying values have also been found for several other oxides, *e.g.*, magnesium oxide 3·07—3·65. Formerly, such variations were attributed to the existence of allotropic modifications of the oxides of different

densities; the oxide prepared in different ways would consist of varying mixtures of these modifications and therefore would show varying densities. Hedvall's investigations of the crystal structure of several oxides (*Arkiv Kem. Min. Geol.*, 1921, **8**, Nr. 11) have shown, however, that this explanation fails in the cases of $Fe_2O_3$, $Al_2O_3$, CoO, $Co_3O_4$, NiO, MgO, ZnO, CuO, and $SnO_2$.* The oxides were prepared by different methods and their densities were compared with those of native oxides. In all cases the same *X*-ray diagram was found, showing conclusively that the difference in the densities of different preparations is in the above cases not due to the presence of varying mixtures of allotropic modifications. These variations are most probably due to the presence of variable amounts of amorphous matter or possibly to hollow spaces or air enclosures in the oxide powder. Accordingly, the highest value is to be considered as the most trustworthy, lying nearest to the "real" density calculated from *X*-ray structure determinations. In the case of ferric oxide, for example, Hedvall determined the structure of the oxide prepared by igniting iron compounds at 600—700°. The oxide was then heated at 1150°, when an appreciable increase in density and a change in colour occurred, and it became "insoluble" in acids; but, as shown by the *X*-ray investigation, the crystal structure remained unchanged.

*Determination of the Density.*—The density of the oxide was determined by weighing a pyknometer of capacity 10·0599 c.c. (1) empty, (2) containing a few (1 to 4) gms. of the oxide, and (3) containing the oxide plus water. The pyknometer containing the oxide was filled with water at about 15° in a vacuum, through a capillary tube, and then placed for some hours in a thermostat kept at 20·00°. The following values were obtained:

$ZrO_2$ prepared from normal sulphate: 5·73, 5·74, 5·72; average 5·73.
$Hf_2O$ " " " " average 9·67 (*X*-ray examination revealed the presence of less than 0·5% $Zr_2O$ in this sample).

The densities of both oxides being known, the percentage of $HfO_2$ in the mixture can be calculated from the formula $x = (d - 5{\cdot}73)/0{\cdot}0394$, where $d$ = density of the oxide mixture at 20°.

The oxides were prepared from the sulphates by driving off the excess of sulphuric acid at 400° and igniting the salt first at a moderate temperature and later at 1000°. The hafnium oxide used was very carefully purified by crystallising the oxychloride several times, then converting it into the sulphate, and subjecting

* *X*-Ray investigations on the yellow and red lead oxides by Kohlschütter and Schetter (*Helv. Chim. Acta*, 1924, **7**, 334) have shown, however, that these are allotropic modifications.

the latter to hydrolysis; the sulphate secured was converted again into the normal sulphate, and the above operation repeated. The zirconium oxide used, which was very carefully purified by similar methods, had been kindly presented to us by Professor O. Hönigschmid, who purified this material in order to determine the atomic weight of zirconium. We found this preparation practically free from hafnium; the trace present was eliminated by very elaborate crystallisation of the potassium double fluorides.

In order to calculate the hafnium content of a preparation from density measurements, it is necessary to prepare the oxides by exactly the same method. Reproducible values are thus obtained; for example, after converting zirconium dioxide ($d$=5·73), prepared from the sulphate, again into this compound and igniting to oxide, the density was 5·75. Oxide prepared from basic sulphate or oxychloride gave lower values:

$d^{20°}$ of $ZrO_2$ prepared from oxychloride, 5·66, 5·67, 5·67; average 5·67.
" " " " basic sulphate, 5·75, 5·75, 5·79, 5·78; average 5·77.
" " " " normal sulphate, 5·90, 5·85, 5·90; average 5·88.

The material used for these measurements was a very pure oxide, but contained about 4% of hafnium dioxide. The basic sulphate was prepared by keeping a solution of the normal sulphate in water (20 parts) at 40° for a few days, when the basic sulphate was precipitated (Hauser, *Z. anorg. Chem.*, 1905, **45**, 194). The above data also explain why such widely varying densities were found for zirconium oxide by different investigators; Venable and Bell (*J. Amer. Chem. Soc.*, 1917, **39**, 1598), preparing their oxide from the oxychloride, found low values (5·49), whilst Nilsson and Petersson (*Ber.*, 1880, **13**, 1460), securing their zirconia by igniting the sulphate, found much higher values (5·85).

To test the accuracy of the density method for the determination of the hafnium content of zirconium, we compared the densities of the above-mentioned preparation, free from hafnium, with a very pure zirconium dioxide containing 1% of hafnium dioxide, and with a third preparation containing 3—4% of hafnium dioxide:

| % $HfO_2$. | Density. | Average. |
|---|---|---|
| 0 | 5·73, 5·72, 5·74 | 5·73 |
| 1 | 5·77, 5·78, 5·76 | 5·77 |
| 4 | 5·85, 5·90, 5·90 | 5·88 |

The different hafnium contents of these preparations are clearly shown by the densities found, indicating that a fair degree of accuracy can be attained by this method.

In carrying out a fractional crystallisation, the progress of the separation of hafnium from zirconium can easily be followed by

density measurements. For example, the values 8·67 (75%), 7·51 (45%), 6·18 (11%) were found for the densities of fractions 1, 6, and 13, respectively. Density measurements can presumably also be used to analyse the tantalum content of a tantalum–columbium mixture (the quantitative determination by other methods is very tedious), for the densities of the two oxides, as in the case of zirconium and hafnium, are sufficiently different to ensure fairly accurate results.

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# CCCXXIII.—*New Halogen Derivatives of Camphor. Part IV. Action of Hydroxylamine on α- and α′-Chlorocamphor and Bromocamphor. Part V. Action of Sodium Methoxide and Ethoxide on αβ-Dibromocamphor. Formation of Esters of α-Bromocampholenic Acid.*

By HENRY BURGESS.

## IV. *Action of Hydroxylamine on α- and α′-Chlorocamphor and Bromocamphor.*

THE action of hydroxylamine acetate upon α-bromocamphor, resulting in the formation of a mixture of camphorquinonedioximes (Angelico, *Atti R. Accad. Lincei*, 1900, [v], **9**, ii, 50) is quite different from its behaviour with β-bromocamphor, which readily forms a monoxime. α- and α′-Chlorocamphor and α′-bromocamphor each gave a mixture from which the same sparingly soluble camphorquinonedioxime could be isolated; the more soluble products were not investigated, since it seemed almost certain, from the large excess of hydroxylamine acetate used, that only dioximes were formed.

The experimental method was as follows: a solution of α-bromocamphor (120 gms. in 300 c.c. of absolute alcohol) was boiled with 96 gms. of hydroxylamine hydrochloride (3·2 mols.) and 150 gms. of anhydrous sodium acetate for 20 hours. The alcohol was evaporated, the sodium hydroxide extract of the residue was filtered from 80 gms. of unchanged α-bromocamphor and acidified slightly, a brown solid (30 gms.), m. p. 120—150°, being obtained. After several crystallisations from alcohol, 5 gms. of β-camphorquinonedioxime, m. p. 240°, were isolated (Angelico, *loc. cit.*, gives m. p. 245°, and Forster, J., 1903, **83**, 525, 248°). The dibenzoyl derivative melted at 188—188·5° (Angelico gives 188°), and the peroxide at 144·5° (Forster, *loc. cit.*).

The product from α-chlorocamphor was characterised by the preparation of the same two derivatives. In the case of the two α′-compounds, since only small quantities were available, the β-camphorquinonedioxime was characterised by the undepressed melting point of its mixture with the dioxime obtained from α-bromocamphor.

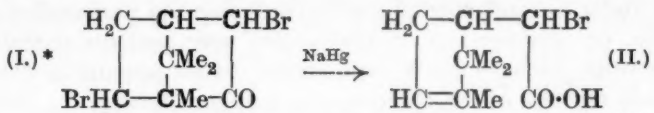
This reaction appears to be a general one for α-halogeno-ketones. Thus chloroacetone readily gives glyoxime (Hantzsch and Wild, *Annalen*, 1896, **289**, 285); methyl αα-dichloroethyl ketone forms diacetyldioxime (Meyer and Jacobsen, "Organische Chemie," I, ii, 880); chloral, with an excess of hydroxylamine in presence of excess of alkali, readily forms chloroglyoxime (Nageli, *Ber.*, 1883, **16**, 499; Hantzsch, *ibid.*, 1892, **25**, 707), whereas, if excess of hydroxylamine hydrochloride in very concentrated aqueous solution is used, chloraloxime is obtained (Meyer, *Annalen*, 1891, **264**, 118).

### V. *Action of Sodium Methoxide and Ethoxide on αβ-Dibromocamphor. Formation of Esters of α-Bromocampholenic Acid.*

During the preparation of α′β-dibromocamphor by the catalytic action of sodium ethoxide on αβ-dibromocamphor (J., 1923, **123**, 1867), an oily by-product was obtained which had the composition of an ethoxybromocamphor. When sodium methoxide was used, the product had the composition of a methoxybromocamphor, although, by a puzzling coincidence, the first samples, which contained the product of a more drastic action, had the composition of an ethoxybromocamphor. When, however, these substances were examined more closely, it seemed quite certain that they could not have this constitution, since they were obviously unsaturated, although they gave no definite products on oxidation; moreover, they could not be converted into the corresponding hydroxybromocamphors by hydrolysis with hydriodic acid, although almost quantitative yields were obtained in determining the methoxy- and ethoxy-groups by Zeisel's method. A clue to the probable nature of the by-products was, however, obtained by comparison with the results of Kachler and Spitzer (*Monatsh.*, 1882, **3**, 205; 1883, **4**, 643), who, on reducing αβ-dibromocamphor with sodium amalgam, obtained a product which they regarded as a hydroxycamphor, but which has since been shown to be an unsaturated acid and has therefore been named α-campholenic acid.* Its formation

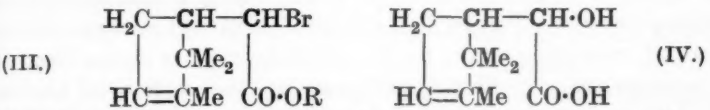
* In order to prevent confusion with α-bromocamphor, etc., this acid is described in the remainder of this paper as "campholenic acid" only. β-Campholenic acid is formed from α-campholenic acid under the influence of strong mineral acids, by an isomeric change which involves the transference of a methyl group and the migration of a double bond; it therefore contains an entirely different ring system, and is only remotely related to camphor.

from αβ-dibromocamphor is represented by the following scheme:



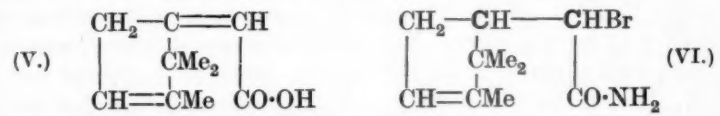

αβ-Dibromocamphor. "α"-Bromocampholenic acid.

The same compound was subsequently obtained by Forster (J., 1902, **81**, 265) by the action of alcoholic potassium hydroxide on β-bromocamphor. The action of sodium alkoxides on αβ-dibromocamphor could therefore be represented as giving rise, by a precisely similar fission of the ring, to a new series of bromocampholenic esters, as shown in formula III.



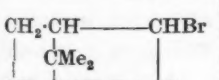

Methyl or ethyl α-bromocampholenate. α-Hydroxycampholenic acid.

This view of the nature of the products of hydrolysis of αβ-dibromocamphor is in complete agreement with their physical and chemical properties, which are those of esters of an unsaturated acid. In particular, they can be hydrolysed by boiling aqueous potassium hydroxide, when they yield a crystalline hydroxy-acid (IV), together with an oily acid, which has not been fully investigated. Since piperidine removes hydrogen bromide from the ester, in preference to forming a piperidide, it is possible that this oily residue may contain the unsaturated, optically inactive acid (V), formed by the removal of hydrogen bromide from the bromo-acid, from which the esters of formula III are derived.




When the esters were acted on by ammonia, a mixed product was formed from which two isomeric compounds having the composition of a bromocampholenamide (VI) were isolated. There can be little doubt that these two compounds are the α- and α′-bromo-derivatives of campholenamide. It is, however, not possible

* Since this work was described, Lipp and Lansberg (*Annalen*, 1924, **436**, 274) have proposed the annexed constitution for αβ-dibromocamphor. This formula does not explain the formation of the bromocampholenic esters so readily as does formula I. Consequently, this constitution will be discussed in a future paper.



at present to say whether the formation of stereoisomerides occurs first under the influence of ammonia during the preparation of the amide, or whether the original esters may perhaps contain two isomerides, such as have been proved to be present in the well-formed crystals of αα′-chlorobromocamphor (Lowry, J., 1898, **73**, 569), and in certain other similar compounds. The widely differing rotatory powers of the two esters (which, however, both obey the simple dispersion law) suggest that two isomerides may be present, but no definite proof of this has yet been obtained.

## Experimental.

*Ethyl α-bromocampholenate*, a colourless oil with a pleasant terpene-like odour, b. p. 140°/15 mm., $d_4^{22°}$ 1·235, which is miscible with all common organic solvents, but is insoluble in water, was obtained as an oil on adding water to the alcoholic mother-liquor from the preparation of α′β-dibromocamphor by the action of sodium ethoxide on αβ-dibromocamphor and was purified by fractional steam distillation followed by three distillations in a vacuum. It was also prepared by the method described in the case of the methyl ester (Found: Br = 29·01; C = 52·72; H = 7·07. $C_{12}H_{19}O_2Br$ requires Br = 29·05; C = 52·36; H = 6·96%).

The compound is neutral to litmus, reduces potassium permanganate immediately in the cold, and rapidly decolorises bromine water. It slowly assumes a brownish-yellow colour on keeping.

*Methyl α-Bromocampholenate.*—Sodium methoxide (45 c.c. of 2·2*N*-solution) was added during ¾ hour to a boiling mixture of 30 gms. of αβ-dibromocamphor with 100 c.c. of methyl alcohol. After refluxing for 5 hours, the methyl alcohol was distilled off through a fractionating column, the distillation being interrupted in order to filter off the precipitated sodium bromide, which was washed with a little ether. The residual oil was distilled twice in a vacuum and came over at 134—135°; yield 86% (Found: C = 50·62; H = 6·50; Br = 30·45. $C_{11}H_{17}O_2Br$ requires C = 50·58; H = 6·56; Br = 30·61%).

(N.B.—In the above preparations, if more than one equivalent of the sodium alkyloxide is used, or if the dibromocamphor is added to the alkali, a mixture of esters, which is not readily separated, is obtained.)

The methyl ester is a colourless liquid, b. p. 134°/14 mm., which resembles the ethyl ester in odour, solubility, tendency to discoloration, behaviour with potassium permanganate and with bromine water. It is very volatile in steam and does not give a colour reaction with ferric chloride.

*α-Hydroxycampholenic Acid.*—After ethyl bromocampholenate

(1 gm.) had been refluxed with 10% aqueous potash (15 c.c.) for 6 hours, one-third of the liquid was distilled off (the distillate gave a strong iodoform-test for ethyl alcohol), and the acidified residue extracted with ether. From the brown oil (0·6 gm.) obtained from the dried extract (sodium sulphate), colourless plates, m. p. 103° (0·3 gm.) were isolated after three crystallisations from hot ligroin; $[\alpha]_{5461}$ — 50° (0·67 gm. per 100 c.c. of chloroform) (Found: C = 65·52; H = 8·83. $C_{10}H_{16}O_3$ requires C = 65·19; H = 8·75%).

By hydrolysing the methyl ester in the same manner, hydroxycampholenic acid, m. p. 103°, $[\alpha]_{5461}$ — 49·5° (2·218 gms. per 100 c.c. of chloroform), was obtained. This shows conclusively that the oily by-products are the ethyl and methyl esters of a bromocampholenic acid.

α-Hydroxycampholenic acid is very soluble in chloroform, acetone, or ether, less so in hot benzene or ligroin, and sparingly soluble in the cold solvents and in water. The acid dissolves in sodium bicarbonate with effervescence, and immediately decolorises bromine water.

The residue which would not crystallise was obviously a mixture of unsaturated acids, formed by the removal of hydrogen bromide from the bromo-acid, but was not investigated fully. It gave a white precipitate with silver nitrate and with lead acetate, and a pale green one with copper acetate. The copper salt is soluble in chloroform, acetone, or ether, giving intense green solutions which, on evaporation, left a sage-green solid, m. p. 201° (decomp.); α-hydroxycampholenic acid, on the other hand, gives a pale blue copper salt, which is insoluble in chloroform, chars at 195°, and melts at 197—198° (decomp.).

*α-Bromocampholenamide.*—A solution of 5 gms. of methyl α-bromocampholenate in 50 c.c. of alcohol was saturated with dry ammonia at 0°, left for a month, and the process repeated. The residue left after distilling off the alcohol was dissolved in ether, and the ethereal solution washed with water. (The washings gave with silver nitrate a copious precipitate of silver bromide. On evaporation of the ether, a pasty solid was left, which, after crystallising many times from ligroin, benzene, and dilute alcohol, gave a main product, m. p. 110—111° (Found: C = 48·66; H = 6·53 $C_{10}H_{16}ONBr$ requires C = 48·78; H = 6·55%). α-Bromocampholenamide crystallises in prisms from ligroin or benzene. It is very soluble in alcohol, ether, acetone, or hot benzene, less soluble in cold benzene or hot ligroin, and sparingly soluble in cold ligroin. It gave $[\alpha]_{5780}$ —29°, $[\alpha]_{5461}$ —32°, $[\alpha]_{4358}$ —54° (0·343 gm. in 15 c.c. of alcohol).

*α′-Bromocampholenamide.*—During the preceding fractional

crystallisations a small quantity of a less soluble isomeride, which is regarded as *α′-bromocampholenamide*, was obtained. This crystallised from alcohol in compact crystals and from ligroin in colourless, transparent, saw-edged rods, m. p. 112·5°; depression on admixture with the α-amide, 12°. It gave $[\alpha]_{5780} + 45°$, $[\alpha]_{5461} + 52°$, $[\alpha]_{4358} + 96°$ in alcohol (0·187 gm. in 15 c.c.). The presence of halogen was indicated by the copper wire test (Found : C = 48·85; H = 6·58%).

A small quantity of another product, m. p. 123°, was separated, but it was insufficient for analysis or investigation.

## Table I.

*Rotatory Dispersions of Methyl and Ethyl Bromocampholenates at 20°.*

Methyl bromocampholenate in benzene (9·9263 gms. in 20·795 gms. of solution; $d_4^{20°}$ 1·0327; 2-dcm. tube; [α] = 1·0143 α).

| λ. | | [α] obs. | [α] calc. | Diff. |
|---|---|---|---|---|
| Li | 6708 | −11·55° | −11·64° | +0·09° |
| Cd | 6438 | −12·78 | −12·78 | ± |
| Zn | 6362 | −13·18 | −13·14 | −0·04 |
| Na | 5893 | −15·64 | −15·71 | +0·07 |
| Cu | 5782 | −16·37 | −16·44 | +0·07 |
| Hg | 5780 | −16·37 | −16·45 | +0·08 |
| Cu | 5700 | −16·93 | −17·01 | +0·08 |
| Ag | 5465 | −18·83 | −18·83 | ± |
| Hg | 5461 | −18·81 | −18·87 | +0·06 |
| Cu | 5218 | −21·07 | −21·11 | +0·04 |
| Ag | 5209 | −21·21 | −21·20 | −0·01 |
| Cu | 5153 | −21·76 | −21·78 | +0·02 |
| Cu | 5105 | −22·19 | −22·29 | +0·10 |
| Zn | 4811 | −25·97 | −25·97 | ± |
| Zn | 4722 | −27·19 | −27·26 | +0·07 |
| Hg | 4358 | −33·58 | −33·89 | +0·31 |

$[\alpha] = 4{\cdot}6078/(\lambda^2 - 0{\cdot}0540)$.

Ethyl bromocampholenate in benzene (11·2915 gms. in 63·705 gms. of solution; $d_4^{20°}$ 0·9261; 6-dcm. tube; [α] = 1·015 α).

| λ. | | [α] obs. | [α] calc. | Diff. |
|---|---|---|---|---|
| Li | 6708 | − 50·81° | − 50·89° | +0·08° |
| Cd | 6438 | − 55·85 | − 55·85 | ± |
| Zn | 6362 | − 57·65 | − 57·37 | −0·28 |
| Na | 5893 | − 68·50 | − 68·40 | −0·10 |
| Cu | 5782 | − 71·26 | − 71·48 | +0·22 |
| Hg | 5780 | − 71·32 | − 71·54 | +0·22 |
| Cu | 5700 | − 73·70 | − 73·92 | +0·22 |
| Ag | 5465 | − 81·82 | − 81·65 | −0·17 |
| Hg | 5461 | − 82·07 | − 81·81 | −0·26 |
| Cu | 5218 | − 91·02 | − 91·25 | +0·23 |
| Cu | 5153 | − 93·96 | − 94·08 | +0·12 |
| Cu | 5106 | − 95·91 | − 96·25 | +0·34 |
| Zn | 4811 | −111·78 | −111·60 | −0·18 |
| Cd | 4700 | −112·13 | −112·21 | +0·08 |
| Zn | 4722 | −117·04 | −116·97 | −0·07 |
| Zn | 4680 | −119·55 | −119·67 | +0·12 |
| Cd | 4678 | −119·66 | −119·80 | +0·14 |
| Hg | 4358 | −144·17 | −144·52 | +0·35 |
| | | Photographic readings. | | |
| Fe | 4415 | −139·51 | −139·29 | −0·22 |
| | 4299 | −149·61 | −149·57 | −0·04 |
| | 4196 | −159·82 | −159·82 | ± |
| | 4101 | −169·98 | −170·28 | +0·30 |
| | 4017 | −180·13 | −180·44 | +0·31 |

$[\alpha] = -20{\cdot}471/(\lambda^2 - 0{\cdot}0480)$.

*Rotatory Dispersions of Methyl and Ethyl Bromocampholenates.*— The rotatory dispersions of the two esters were measured at 20° in purified benzene. The rotations given in Table I are seen to obey the simple dispersion law. This result was unexpected, since, although active alcohols and ethers nearly always show simple rotatory dispersion, most of their esters exhibit complex dispersion (Hunter, this vol., p. 1198; compare Hall, J., 1923, **123**, 105). Complex dispersion was also observed by Wood, Such, and Scarf (J., 1923, **123**, 600) in the alkyl esters of *d*-lactic acid, where the asymmetric carbon atom is in the acid radical instead of in the alkyl group. The *l*-menthyl esters of the saturated dicarboxylic acids, however, show simple dispersion (Hall, *loc. cit.*), and other esters which are

complex when heated show simple dispersions at lower temperatures, so that the result recorded above, although unexpected, is not without precedent.

My thanks are due to Prof. T. M. Lowry for valuable help and advice, and to the Royal Commissioners of the Exhibition of 1851 for the renewal of a scholarship which enabled me to carry out this work.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, July 17th*, 1924.]

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## CCCXXIV.—*The System Sodium Carbonate–Sodium Sulphate–Water.*

By WILLIAM AUGUSTUS CASPARI.

THE system sodium carbonate–sodium sulphate–water and its extensions have an interest comparable with that of the much more complicated systems involved in the evaporation of sea-water. Unlike waters of the oceanic type, many river and lake waters hold in solution a clear excess of alkali and tend on concentration to eliminate calcium and magnesium by precipitation, whilst potassium is removed by adsorption. When the crystallising point is approached, such waters are in the main solutions of sodium carbonate, bicarbonate, sulphate, and chloride. It is in this way that soda lakes were formed, and continue to be formed at the present day, and that deposits of natron, mirabilite, thenardite and related minerals were laid down in former epochs. In the arts, moreover, the system sodium carbonate–sodium sulphate–water frequently occurs, as, for instance, when a base or carbonate has been precipitated from sulphate solution and the filtrate is concentrated for purposes of recovery.

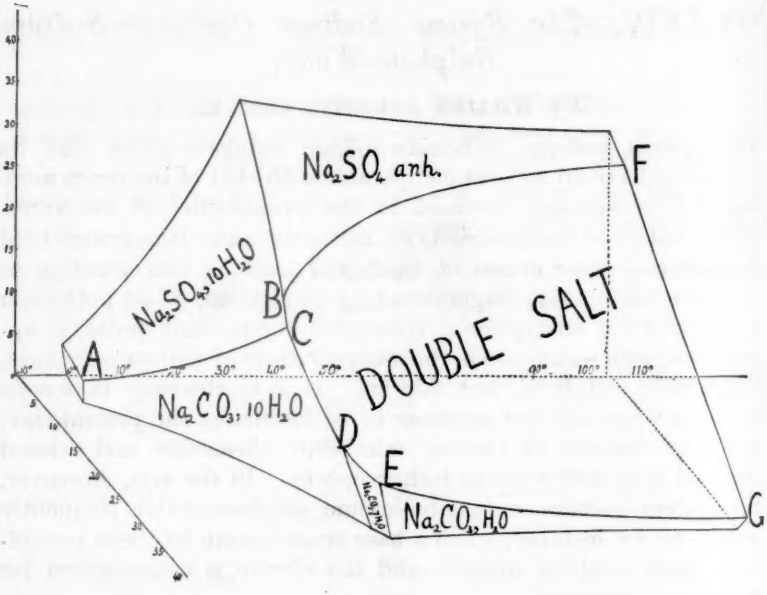
The binary system sodium sulphate–water has been studied by Loewel and more recently by Berkeley (*Phil. Trans.*, 1904, **203**, 189); the system sodium carbonate–water by Mulder and, with special reference to the transition region, by Wells and McAdam (*J. Amer. Chem. Soc.*, 1907, **29**, 721). The results of the present investigation may by anticipation be stated as follows:

1. Up to 26°, solid phases consist of the decahydrates of both salts throughout. The isothermal solubility curves are of the simplest character, and each branch is not far from rectilinear. The effect of one salt on the solubility of the other is much the same and is comparatively small; the maximum amount of either salt extruded from solution by 1 mol. of the other ranges from 0·2 mol. to 0·4 mol.

At the points where both decahydrates are in equilibrium there are in solution from 3·2 mols. to 1·5 mols. of $Na_2CO_3$ per mol. of $Na_2SO_4$, the ratio diminishing as the temperature rises.

2. Isodimorphous solutions (mixed crystals) of carbonate decahydrate in sulphate decahydrate, and *vice versa*, crystallise from mixed solutions. The highest observed concentrations of the one solid in the other were: in sodium sulphate decahydrate, 100 mols. $Na_2SO_4$ : 7·3 mols. $Na_2CO_3$, in sodium carbonate decahydrate, 100 mols. $Na_2CO_3$ : 5·0 mols. $Na_2SO_4$.

3. At and above the transition temperature, 26·1°, an anhydrous double salt, $Na_2CO_3,2Na_2SO_4$, appears, and this salt occupies a wide




field of stability up to the boiling point, but the double salt $Na_2CO_3,4Na_2SO_4$, obtained by Schulten (*Compt. rend.*, 1896, **123**, 1325) from highly caustic solutions, was not encountered. From 67° upwards, $Na_2CO_3,2Na_2SO_4$ is stable in contact with its own solution.

*Joint Solubilities.*—Isotherms were determined at 20°, 25°, 30°, 35°, 50°, and 75° by means of bottles rotated in a thermostat. In all cases the bottles were charged with decahydrates of the two salts, recrystallised until free from chloride; up to 30°, small quantities of water had to be added, at higher temperatures this was superfluous. Eight to ten points were determined along each curve, and additional closer points were taken where necessary. The densities of all the solutions were measured pyknometrically.

Isolation of the solid phases proved a simple matter in the decahydrate region, where the crystals could be washed without decomposition. At higher temperatures, however, the only practicable procedure was to filter off the microcrystalline solid phase and press without washing between absorbent paper, all as expeditiously as possible.

For the solubilities of sodium carbonate alone and sodium sulphate alone, the data in Seidell's tables were taken. The densities of carbonate solutions were calculated from Wegscheider's formula (*Monatsh.*, 1905, **26**, 685), those of sulphate solutions were interpolated from Berkeley's figures.

On plotting the isothermal curves, it was found that the branches along which $Na_2SO_4,10H_2O$ is the solid phase have but a slight concavity, whilst the concavities of all other isotherm segments are so small as to be scarcely distinguishable, within the accuracy of the determinations, from linearity. It may suffice, therefore, to state only the multiple points and end-points belonging to each isotherm, as is done in the subjoined tables. The solid phases (consisting of an unmixed salt) in contact with any liquid of intermediate composition can be inferred from column C.

A. Gms. of salt in 100 gms. of saturated solutions. B. Gm.-mols. per litre. C. Solid phases.

| | A. | | B. | | C. |
|---|---|---|---|---|---|
| Temp. | $Na_2CO_3$. | $Na_2SO_4$. | $Na_2CO_3$. | $Na_2SO_4$. | |
| 15° | 0 | 11·8 | 0 | 0·93 | $Na_2SO_4,10H_2O$. |
| | 12·3 | 8·0 | 1·43 | 0·70 | $Na_2SO_4,10H_2O$; $Na_2CO_3,10H_2O$ |
| | 14·1 | 0 | 1·55 | 0 | $Na_2CO_3,10H_2O$. |
| 20° | 0 | 16·25 | 0 | 1·32 | $Na_2SO_4,10H_2O$. |
| | 14·95 | 11·2 | 1·80 | 1·00 | $Na_2SO_4,10H_2O$; $Na_2CO_3,10H_2O$. |
| | 17·75 | 0 | 1·99 | 0 | $Na_2CO_3,10H_2O$. |
| 25° | 0 | 21·9 | 0 | 1·86 | $Na_2SO_4,10H_2O$. |
| | 17·9 | 16·2 | 2·29 | 1·55 | $Na_2SO_4,10H_2O$; $Na_2CO_3,10H_2O$. |
| | 22·6 | 0 | 2·68 | 0 | $Na_2CO_3,10H_2O$. |
| 30° | 0 | 29·3 | 0 | 2·67 | $Na_2SO_4,10H_2O$. |
| | 10·2 | 25·1 | 1·30 | 2·38 | $Na_2SO_4,10H_2O$; $Na_2SO_4$ (anh.). |
| | 15·5 | 19·5 | 2·00 | 1·88 | $Na_2SO_4$; double salt. |
| | 25·8 | 8·6 | 3·32 | 0·83 | Double salt; $Na_2CO_3,10H_2O$. |
| | 27·15 | 0 | 3·48 | 0 | $Na_2CO_3,10H_2O$. |
| 35° | 0 | 33·15 | 0 | 3·10 | $Na_2SO_4$ (anh.). |
| | 14·3 | 20·6 | 1·83 | 1·97 | $Na_2SO_4$; double salt. |
| | 30·0 | 5·7 | 3·90 | 0·56 | Double salt; $Na_2CO_3,7H_2O$. |
| | 33·0 | 0 | 4·26 | 0 | $Na_2CO_3,7H_2O$. |
| 50° | 0 | 31·8 | 0 | 2·93 | $Na_2SO_4$ (anh.). |
| | 11·4 | 22·2 | 1·43 | 2·08 | $Na_2SO_4$; double salt. |
| | 29·7 | 5·5 | 3·80 | 0·53 | Double salt; $Na_2CO_3,H_2O$. |
| | 32·2 | 0 | 4·10 | 0 | $Na_2CO_3,H_2O$. |
| 75° | 0 | 30·4 | 0 | 2·72 | $Na_2SO_4$ (anh.). |
| | 7·6 | 24·2 | 0·93 | 2·16 | $Na_2SO_4$; double salt. |
| | 29·0 | 4·8 | 3·72 | 0·46 | Double salt; $Na_2CO_3,H_2O$. |
| | 31·45 | 0 | 3·93 | 0 | $Na_2CO_3,H_2O$. |

*Cryohydric Points.*—For sodium sulphate, the temperature —1·2° and composition 3·85% of $Na_2SO_4$ were taken from Coppet (*Z. physikal. Chem.*, 1897, **22**, 239). For sodium carbonate, both Coppet and Guthrie give —2·1° as the temperature; but since there is a discrepancy between their concentrations, this datum was redetermined and found to be 5·75%, the temperature —2·1° being confirmed. Determination of the joint cryohydric point, starting from solutions of varied concentrations and with due precautions against supersaturation, gave the following results (point A): Temperature —2·45°, $Na_2CO_3$ 5·21%, $Na_2SO_4$ 2·06%.

*Boiling Points of Saturated Solutions.*—For sodium sulphate, we have temperature 102·9° (Berkeley and Applebey, *Proc. Roy. Soc.*, 1911, *A*, **85**, 489), concentration 29·6% of $Na_2SO_4$, and density 1·245. Boiling-point data for sodium carbonate monohydrate, the published values being somewhat uncertain, were specially redetermined, with the following results: Temperature 104·6°, concentration 31·2% of $Na_2CO_3$, density 1·295.

Passing on to the ternary system, the two quadruple points were determined as follows. Saturated solutions of the two salts were mixed in the ratios 1 : 10 and 10 : 1, respectively. The solvent was evaporated by boiling in a wide test-tube having a tubulure, a little steam being at the same time passed in, until a considerable deposit had been precipitated. Heating by means of steam alone was then continued until the temperature became constant. The liquid and solid phases were dealt with as usual. In a series of experiments, more and more solvent was distilled until the carbonate precipitate was contaminated with decidedly more sulphate than could have been due to mother-liquor, and *vice versa*. These points were taken to be the breaks in the boiling-point curve, namely:

| | B. p. | *d*. | $Na_2CO_3$%. | $Na_2SO_4$%. | Solid phase. |
|---|---|---|---|---|---|
| Point F. | 103·0° | 1·249 | 4·7 | 25·2 | $Na_2SO_4$; double salt. |
| „ G. | 104·8 | 1·301 | 28·1 | 4·5 | $Na_2CO_3,H_2O$; double salt. |

*Transition Points.*—Between the isotherms for 25° and 30° there are two transition points, where the solid phases are $Na_2CO_3,10H_2O$, $Na_2SO_4,10H_2O$, double salt, and $Na_2SO_4,10H_2O$, $Na_2SO_4$(anh.), double salt, respectively. The former was determined by observing mixtures at increasing temperatures, until a solid phase consisting of large soda and Glauber's salt crystals broke down into the pulverulent double salt. This change is readily visible, and, moreover, is accompanied by a considerable shrinkage in the bulk of the solid phase. Care was taken that eventually there should be crystals of both decahydrates present. Thus, at 26·0°, after the mixture had been kept for several days in the

thermostat, the solid phase consisted of the two decahydrates only. At 26·1° there began to be formed, after some hours, a pulverulent admixture of double salt. The solution then contained 19·0% of $Na_2CO_3$ and 17·6% of $Na_2SO_4$ (point C).

The temperature of transition to anhydrous sodium sulphate was located by bringing small crystals of both decahydrates into equilibrium near the $Na_2SO_4$–double salt quadruple point, at a series of temperatures. On analysing the solid phases, the change from $Na_2SO_4,10H_2O$ to $Na_2SO_4$ anh. was found to take place at 27·3°, the composition of the liquid being 16·3% of $Na_2CO_3$ and 19·3% of $Na_2SO_4$ (point B). The short stretch of curve, then, along which double salt and sulphate decahydrate are joint solid phases is confined to little more than 1°, but covers a considerable change in the composition of the liquid phase.

Between 30° and 40°, at the carbonate end of the isotherms, there are two transition points where $Na_2CO_3,10H_2O$ changes to $Na_2CO_3,7H_2O$ and then to $Na_2CO_3,H_2O$, in presence of double salt. These were fixed by a series of equilibrium determinations, with careful analysis of the solid phases. The lower transition temperature is at 30·5° (point D; $Na_2CO_3$ 26·2%, $Na_2SO_4$ 8·3%), the higher at 35·7° (point E; $Na_2CO_3$, 30·1%, $Na_2SO_4$ 5·65%). The temperature range within which sodium carbonate heptahydrate is stable with water alone (32—35°) is thus slightly opened out.

The requisite data now being available, the complete diagram for the system between ice points and boiling points has been drawn up in three-dimensional rectangular co-ordinates, and is shown in the figure on p. 2382. It will be seen that above approximately 30°, double salt is the dominant solid phase; hence evaporation of mixed solutions, unless conducted below 26°, can at best yield only moderate proportions of single salts, and very little single salt as the boiling point is approached. Natural occurrences of double salt do not appear to have been reported. Should such deposits be found, we may take it that they could not have formed below 26°; that if accompanied by relatively large amounts of carbonate or sulphate they were probably laid down between 26° and 40°; and that deposits of double salt with little admixture indicate evaporation at higher temperatures.

*Sodium Carbonate–Sulphate.*—The double salt may be isolated as a crystalline powder by boiling down a solution of the components in the molecular ratio 2 : 1, or by salting out a hot saturated solution with sodium acetate. On slow evaporation of 2 : 1 solutions above 70°, or of 3 : 2 solutions at 40—50°, a hard, thin crust of double salt forms on the surface, whilst crystals of substantial size separate at the bottom. These unite to stellate bundles of thick prisms or to

hard, cauliflower-like aggregates, $d$ 2·59 (Found: $Na_2CO_3 = 26·73$, 27·66, 26·45; $Na_2SO_4 = 73·45$, 72·26, 73·42. $Na_2CO_3,2Na_2SO_4$ requires $Na_2CO_3 = 27·16$; $Na_2SO_4 = 72·84\%$).

In dry weather the salt remains unaffected by exposure to air, but in moist air it deliquesces to an oily liquid from which either sulphate or carbonate decahydrate may be crystallised on addition of the proper nucleus.

The upper limit of the transition interval, which occurs between 50° and 75° (column B in the table on p. 2383), is found, by graphic interpolation, to lie at 67°. Above 67°, then, the salt is stable in contact with its own solution. Between 26° and 67°, a solution in which the molecular ratio is 2 : 1 begins to deposit sulphate alone on evaporation; and, conversely, the double salt, when leached with small amounts of water, leaves a residue of sulphate. Below 26°, the double salt is unstable in contact with water; thus, under the microscope, fragments of double salt are seen, soon after they are surrounded with water, to send out prisms of sodium sulphate decahydrate. Pulverulent double salt mixed with a little water sets to a hard, translucent cement consisting of the two decahydrates.

*Solid Solutions.*—In the decahydrate region, the crystals in contact with mixed solutions are not pure, but contain isodimorphous admixtures of the opposite salt. When allowed to separate, by cooling, from clear solutions at rest or under very gentle agitation, the crystals are large enough to permit of thorough washing with cold water before being analysed. The compositions of a series of crystals and of the solutions in contact are tabulated below. Under molecular partition are shown the ratios of the concentrations in the liquid (gm.-mols. per litre) to those in the crystal (gm.-mols. per litre); for the calculation of the latter, the densities 1·45 and 1·48 were accepted for soda crystal and Glauber's salt, respectively.

| $Na_2CO_3$ % in the liquid. | $Na_2CO_3$ % in Glauber crystals. | Molecular partition. | $Na_2SO_4$ % in the liquid. | $Na_2SO_4$ % in soda crystals. | Molecular partition. |
|---|---|---|---|---|---|
| 2·6 | 0·29 | 7·2 | 2·7 | 0·38 | 6·1 |
| 4·3 | 0·47 | 7·6 | 5·6 | 0·77 | 6·1 |
| 10·0 | 1·27 | 6·6 | 8·9 | 1·30 | 5·6 |
| 13·6 | 1·62 | 8·1 | 11·0 | 1·62 | 5·9 |
| 14·9 | 1·80 | 6·9 | 16·1 | 2·34 | 6·3 |
| 17·8 | 2·27 | 7·5 | | | |

It will be seen that in both series the partition coefficients are fairly constant for simple molecules, but that the coefficient for sodium carbonate as solute is slightly higher than that for sodium sulphate. The percentages at the bottom of the middle columns may be taken as being close upon the maximum limits of solid solubility, since they were determined at the quadruple point of the 25° isotherm; a

transition point supervenes shortly above this temperature, and thenceforward the decahydrates are nowhere in contact with more favourable concentrations of the opposite salt.

UNITED ALKALI COMPANY,
WIDNES.

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# CCCXXV.—*Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. Part I. Mixtures of Air and One Gas at the Ordinary Temperature and Pressure.*

By ALBERT GREVILLE WHITE.

NUMEROUS determinations have been made during the last fifty years of the limits for the propagation of flame in gas–air mixtures, but concordant results have been obtained by different workers only in recent years. Earlier work was concerned mainly with methane, hydrogen, and carbon monoxide, but limits are now given also for ammonia (J., 1922, **121**, 1688), methane, pentane, ethylene, propylene, butylene, acetylene, and hydrogen sulphide. Parts II and III will deal with the limits for mixtures containing more than one inflammable gas, and with the effect of temperature on the limits. Existing data are as follows :

*Carbon monoxide.*

14·3—16·7 to 75—80 [1]
14·1—14·3 to 74·6—74·8 [2]
13 to 75 [3]
15·8—16·0 to 72·5—76·5 [4]
U. 14·4 to — [5]
D. 16·4—16·6 to 74·8—75·1 [5]
D. 16·5 to 74·95 [6]
15·9 to 72·9 [7]
U. 12·5 to 73·0—74·2 [8]
12·6 to 70 [9]
C. 15·0 to 73 [10]
D. 15·6 to 70·9 [11]
C. 15·40 to 71·60 [12]

*Hydrogen Sulphide.*

4·5 to 19·0 [9]
H. 5·9 to 27·2 [26]

*Ethane.*

3·10 to — [27]
C. 3·4 to 10·7 [18]
3·1 to 10·7 [9]
C. 2·5 to 5·0 [10]
H. 3·3 to 10·6 [18]
D. 4·2 to 9·5 [11]
D. 3·13 to 9·85 [25]

*Acetylene.*

3 to 82 [3]
2·8 to 65·0 [29]
D. 3·35 to 52·3 [6]
1·53—1·77 to 57·95—58·65 [17]
U. 2·53 to 73 [30]
D. 2·87 to — [30]
3·0 to 46·0 [9]
C. 3·0 to 73·0 [10]
D. 3·5 to 52·3 [11]
C. 2·39 to (undefined) [12]

*Hydrogen.*

7·7—8·3 to 50—60 [1]
6 to 80 [13]
7 to 75 [14]
9·2—9·5 to 64·7—65·0 [2]
5 to 72 [3]
6·3 to 80 [15]
10 to — [16]
U. 4·5 to — [5]
D. 9·45 to 66·4 (19 mm.) [6]
D. 8·5 to — (62 mm.) [6]
D. 9·73—9·96 to 62·75—63·58 [17]
9·0 to 68·5 [7]
U. 4·1 to 71·5—74·2 [8]
4·1 to 60 [9]

*Hydrogen* (contd.).

C. 10·0 to 66 [10]
U. 4·2 to — [18]
D. 9·7 to — [18]
C. 9·42 to 65·9 [12]
D. 9·5 to 65·2 [11]

*Pentane.*

1·1 to — [16]
D. 2·4 to 4·9 (19 mm.) [6]
D. 1·3 to — (62 mm.) [6]
1·37 to — (*n*-) [27]
1·32 to — (*iso*-) [27]
C. 1·4 to 4·5 [18]
1·35 to 4·5 [9]
H. 1·6 to 5·4 [18]
D. 1·75 to 4·68 [25]

*Methane.**

3·20—3·67 to 7·46—7·88 [17]
2·50 to — [19]
5·5 to 12·8 [21]
U. 5·20 to — [20]
D. 5·76 to — [20]
6·0 to 13·0 [7]
U. 5·3 to 15·1—15·4 [8]

*Methane* (contd.).

C. 5·77 to — [22]
U. 5·4 to 14·8 [23]
D. 6·0 to 13·4 [23]
U. 4·9—5·0 to 15·0—15·4 [24]
D. 5·4—5·8 to 13·5—13·9 [24]
5·6 to 14·8 [9]
C. 5·5 to 14·5 [10]
U. 5·5 to — [18]
D. 6·1 to — [18]
D. 6·2 to 11·9 [11]
U. — to 14·28 [25]
D. 5·80 to 13·38 [25]
C. 5·82 to 13·60 [13]

*Ethylene.*

4 to 22 [3]
D. 4·1 to 14·6 (19 mm.) [6]
D. 3·4 to — (62 mm.) [6]
5·7 to 17·5 [9]
D. 4·0 to 14·0 [11]
U. 3·3 to 25·6 [26]
D. 3·6 to 13·7 [23]
C. 3·34 to (undefined) [12]

*Propylene.*

H. 2·6 to 7·4 [28]

U, H, and D indicate that the limits concerned have been determined for propagation upwards, horizontally, and downwards, respectively. C indicates that central ignition was used.

* For methane limits published prior to 1913, see Third Report of Explosions in Mines Committee.

[1] Wagner, Bayerisches Industrie und Gewerblatt, 1876, **8**, 186. [2] Roszkowski, *Z. physikal. Chem.*, 1891, **7**, 485. [3] Clowes, *J. Soc. Chem. Ind.*, 1896, **15**, 701. [4] Le Chatelier and Boudouard, *Compt. rend.*, 1898, **126**, 1344. [5] Eitner, Habilitationsschrift, München, 1902. [6] Eitner, *J. Gasbeleucht.*, 1902, **45**, 2, 21, *et seq.* [7] Terres and Plenz, *J. Gasbeleucht.*, 1914, **57**, 995, *et seq.* [8] Coward and others, J., 1914, **105**, 1859; 1919, **115**, 27. [9] Thornton, *Phil. Mag.*, 1917, [vi], **33**, 190. [10] Burrell and Gauger, Tech. Paper 150, Bureau of Mines, 1917. [11] Terres, *J. Gasbeleucht.*, 1920, **63**, 785, *et seq.* [12] Berl and Fischer, *Z. Elektrochem.*, 1924, **30**, 29. [13] Mallard and Le Chatelier, *Ann. Mines*, 1883, [viii], **4**, 347. [14] Broockmann, *J. Gasbeleucht.*, 1889, **32**, 189. [15] Bunte, *Ber.*, 1898, **31**, 19. [16] Le Chatelier and Boudouard, *Compt. rend.*, 1898, **126**, 1510. [17] Teclu, *J. pr. Chem.*, 1907, [ii], **75**, 212. [18] Payman, J., 1919, **115**, 1436. [19] Perman, *Nature*, 1911, **99**, 2013. [20] Leprince-Ringuet, *Compt. rend.*, 1914, **158**, 1793. [21] Clement. Tech. Paper 43, Bureau of Mines, 1913. [22] Parker, J., 1914, **105**, 1002. [23] Burgess and Wheeler, J., 1914, **105**, 2591. [24] Burrell and Oberfell, Tech. Paper 119, Bureau of Mines, 1915. [25] Payman and Wheeler, J., 1923, **123**, 426. [26] Jones, Yant, and Berger, *Ind. Eng. Chem.*, 1924, **16**, 353. [27] Wheeler, J., 1911, **99**, 2013. [28] Chapman, J., 1921, **119**, 1677. [29] Le Chatelier, *Compt. rend.*, 1895, **121**, 1144. [30] Burrell and Oberfell, Tech. Paper 112, Bureau of Mines, 1915.

Discrepancies in the earlier values may be ascribed (I) to the use of vessels too narrow to eliminate the effects of wall conduction

or too short to give certain information as to whether a given mixture would propagate flame indefinitely, (II) to weak ignition, (III) to the use of various directions of propagation, giving greater discrepancies at the lower limit for hydrogen than for methane or carbon monoxide, (IV) to incomplete mixing (see Teclu's figures for methane and acetylene), (V) to the use of an unsuitable vessel and an unsatisfactory criterion of propagation in Perman's work on methane. Thornton's figure for ethylene is anomalous; and the values of Terres are likely to be low on account of his use of a narrow (19 mm.) tube. Chapman and Payman used 25 mm. tubes, whilst the values of Payman and Wheeler, with the exception of those for methane, are for 20 mm. tubes. The results of Berl and Fischer are "explosion limits," and were determined in a spherical glass vessel 27 mm. in diameter. The vessel used was too small to give sound values for limits for the propagation of flame, as is shown by figures given by these authors for the effect of different sparks on the limits determined in a pipette, presumably of similar dimensions.

*Results.*

Although most of the preliminary work carried out on vapour–air mixtures (J., 1922, **121**, 1244) would probably apply to gas–air mixtures with little modification, it was thought advisable to examine roughly the effect of moisture content on the lower limit of one of the gases. The gas chosen was carbon monoxide, for obvious reasons. Whilst the lower limit for downward propagation in a 5 cm. tube in a mixture containing 1% of moisture was 15·7%, the limit in a mixture roughly dried by fairly rapid bubbling through 98% sulphuric acid was 16·5%, whilst for a mixture very carefully dried with the same acid the value found for the limit was 18·0%. These figures showed that limit determinations in dry carbon monoxide–air mixtures were likely to give some trouble. It was accordingly decided to carry out the whole of the work with mixtures containing 1% of moisture, though this figure was modified later for upper limit mixtures containing carbon monoxide. The propagation ranges found are shown in Table I.

Two values are given for the lower limit for propagation upwards in hydrogen–air mixtures in a 7·5 cm. tube. The lower value shows the minimum quantity that would propagate flame from one end of the tube to the other under these conditions. In this case, the flame, which consisted of one or more small balls, diminished in size throughout its path, and would certainly have failed to traverse a similar tube a metre longer. The higher value shows the minimum quantity of hydrogen that gave an observer the impression that it would propagate flame indefinitely. Owing to ignition difficulties,

TABLE I.

Showing the ranges that would propagate flame in different gas–air mixtures in glass tubes of various diameters.

The original temperature of the gas mixture was $17° \pm 3°$.

| | Direction of Propagation. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | U. | H. | D. | U. | H. | D. | U. | H. | D. |
| | 7·5 cm. tube. | | | 5·0 cm. tube. | | | 2·5 cm. tube. | | |
| Hydrogen | 4·15 (4·00) to 75·0 | 6·50 to — | 8·8 to 74·5 | 4·15 to 74·5 | 6·70 to — | 9·0 to 74·0 | 4·25 to 73·0 | 7·15 to — | 9·4 to 71·5 |
| Carbon monoxide | 12·8 to 72·0 | 13·6 to — | 15·3 to 70·5 | 13·1 to 72·0 | 14·1 to — | 15·7 to 70·5 | 13·2 to 71·0 | 15·9 to — | 16·3 to 70·0 |
| Hydrogen sulphide | 4·30 to 45·5 | 5·30 to 35·0 | 5·85 to 21·3 | 4·40 to 44·5 | 5·40 to 26·6 | 6·05 to 19·8 | | | |
| Methane | 5·35 to 14·85 | 5·40 to 13·95 | 5·95 to 13·35 | 5·40 to 14·25 | 5·65 to 13·95 | 6·12 to 13·25 | 5·80 to 13·20 | 6·20 to 12·90 | 6·30 to 12·80 |
| Ethane | 3·12 to 14·95 | 3·15 to 12·85 | 3·26 to 10·15 | 3·15 to 14·8 | 3·22 to 11·75 | 3·32 to 10·0 | | | |
| *n*-Pentane | 1·42 to 8·0 | 1·44 to 7·45 | 1·48 to 4·64 | 1·43 to 8·0 | 1·46 to 6·70 | 1·49 to 4·56 | | | |
| Ethylene | 3·02 to >34·0 | 3·20 to 23·7 | 3·33 to 15·5 | 3·13 to 33·3 | 3·25 to 22·4 | 3·42 to 15·3 | 3·15 to 27·6 | 3·30 to 14·0 | 3·45 to 13·7 |
| Propylene | 2·18 to 9·7 | 2·22 to 9·3 | 2·26 to 7·40 | 2·21 to 9·6 | 2·26 to 8·4 | 2·29 to 7·2 | | | |
| Butylene | 1·70 to 9·0 | 1·75 to 9·0 | 1·80 to 6·25 | 1·80 to 9·0 | 1·82 to 7·4 | 1·84 to 6·10 | | | |
| Acetylene | 2·60 to >80·5 | 2·68 to >78·5 | 2·78 to 71·9 | 2·60 to 78·0 | 2·68 to 68·5 | 2·80 to 63·5 | 2·73 to 70·0 | 2·87 to 59·5 | 2·90 to 55·0 |

the precise limit figure was not determined in three cases—one for ethylene and two for acetylene. In each case, however, the actual limit is believed to be quite near to the figure given.

The results agree generally with those of Coward and his collaborators (*loc. cit.*), who used larger vessels but dealt only with upward propagation, and (allowing for the size of the vessels used by these workers) with those of Chapman, of Payman, of Payman and Wheeler, and also with those of Burrell and Oberfell, except for methane at the lower limit, where the values of the American workers are probably too low. The ranges given by Terres are generally too narrow, and Thornton's value for the lower limit of ethylene is

certainly wrong. It is difficult to account for the discrepancy between the author's results and those of Jones, Yant, and Berger for hydrogen sulphide. It may be due to the fact that the tube used by the American workers was open to the air, but the author's previous experience with a tube similar to theirs would not lead him to expect such differences.

*Discussion of Results.*

The lower limit values determined in 5 cm. and in 7·5 cm. tubes do not differ greatly, giving support to the conclusion arrived at from a consideration of vapour–air results (J., 1922, **121**, 1244), that wall-cooling has little influence on the results obtained in 7·5 cm. glass tubes. The marked difference found when using 5 cm. and 7·5 cm. tubes for the determination of the upper limit for horizontal propagation in hydrogen sulphide–air mixtures is presumably to be ascribed to the increased convection effect in the larger tube. A similar, although smaller effect is found for propylene, butylene, and pentane. The most interesting variation of limit with diameter of tube is obtained with acetylene–air mixtures at the upper limit for downward propagation. Convection may be partly responsible for the unusually large differences found, but the sensitiveness of acetylene to pressure must not be overlooked in this connexion. The preliminary compression to which the unburnt mixture is subjected during the progress of the flame in a limit tube is certainly considerably greater for a 7·5 cm. than a 5·0 cm. tube, particularly during the determination of an upper limit, and it is probable that the upper-limit results obtained for acetylene–air mixtures are in no way comparable with those determined under constant pressure conditions. It will also be observed that the effect of direction of propagation on lower-limit results is often greater for gas–air mixtures than for normal vapour–air mixtures.

A comparison of the results of determinations of the limits for the propagation of flame in twelve vapour–air mixtures (White, *loc. cit.*) showed that for all but one of these vapours certain approximate relations existed between the limits found for any one vapour. Thus for downward propagation the upper limit generally contained about 3·5 times as much combustible vapour as the lower limit. It is evident that such a relation as this could not possibly be general, as in the case of a vapour which only just burns in air the amount of combustible in the upper- and lower-limit mixtures would be practically the same. Again, for any mixture it is only to be expected that the ratio of the upper to lower limit found should vary with the temperature at which the limits are determined. The vapours examined almost all appeared to correspond from the

temperature point of view, as was sufficiently evidenced by the calorific value relation connecting the figures found for the lower limits in air. In these circumstances, it is of interest to examine how gases compare when subjected to a similar examination. This is done in Table II.

This table also shows the calorific value of each of the lower-limit mixtures that will just propagate flame downwards. In other columns are shown the theoretical flame temperatures attained at the limits, the values taken for the specific heats (at constant pressure) of nitrogen, carbon dioxide, and steam, being those of Holborn and Henning (*Ann. Phys.*, 1905, [iv], **18**, 739; 1907, [iv], **23**, 809). For the other products of conbustion and the combustible gases, the values used were those of Lewis and Randall (*J. Amer. Chem. Soc.*, 1912, **34**, 1128). No correction has been made for loss of heat.

TABLE II.

Showing:

(*a*) The calorific value of the various lower-limit mixtures;

(*b*) The theoretical flame temperatures attained in various gas–air limit mixtures;

(*c*) Certain relations between the upper and lower limits for the same gas mixture.

The limits given are for propagation downward in 7·5 cm. tubes, the gas–air mixture being originally at $17° \pm 3°$. Owing to the fact that ammonia–air mixtures do not propagate flame downwards at the ordinary temperature, the ammonia values are for horizontal propagation.

| | Net calorific value. $C$. | Lower limit downwards. $L_1$. | Upper limit downwards. $L_2$. | $L_1 \times C$. | $L_2/L_1$. | Theoretical flame temperature. Lower limit. | Theoretical flame temperature. Upper limit. | Mixture for combustion to $CO_2$ & $H_2O$. $M_1$. | Mixture for combustion to CO & $H_2O$. $M_2$. | $M_1+M_2$ or $2M_1$. | $L_1+L_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Carbon monoxide | 68 | 15·3 | 70·5 | 1040 | 4·6 | 1410° | 1100° | 29·6 | — | 59·2 | 85·8 |
| Hydrogen | 57 | 8·8 | 74·5 | 502 | 8·5 | 765 | 875 | 29·6 | 29·6 | 59·2 | 83·3 |
| Ammonia | 73·5 | 17·4 | 26·3 | 1279 | 1·5 | 1580 | 1715 | 21·9 | 21·9 | 43·8 | 43·7 |
| Hydrogen sulphide | 126 | 5·85 | 21·3 | 737 | 3·6 | 1040 | | 12·3 | 12·3 | 24·6 | 27·1 |
| Methane | 190 | 5·95 | 13·35 | 1131 | 2·2 | 1465 | | 9·5 | 12·3 | 21·8 | 19·3 |
| Ethane | 337 | 3·26 | 10·15 | 1099 | 3·1 | 1410 | | 5·66 | 7·75 | 13·4 | 13·4 |
| *n*-Pentane | 780 | 1·48 | 4·64 | 1154 | 3·1 | 1450 | | 2·56 | 3·68 | 6·2 | 6·1 |
| Ethylene | 315 | 3·33 | 15·5 | 1049 | 4·7 | 1380 | | 6·54 | 9·5 | 16·0 | 18·8 |
| Propylene | 460 | 2·26 | 7·40 | 1040 | 3·3 | 1355 | | 4·46 | 6·54 | 11·0 | 9·7 |
| Butylene | 606 | 1·80 | 6·25 | 1091 | 3·5 | 1400 | | 3·38 | 4·99 | 8·4 | 8·1 |
| Acetylene | 301 | 2·78 | 71·0 | 837 | 26 | 1155 | | 7·75 | 12·3 | 20·0 | 73·8 |

A glance at Table II shows that the regularities found for vapours are much less marked for the gases examined, and often seem to disappear altogether. Thus the ratio $L_2/L_1$ was found to be roughly 3·5 for vapours, but in Table II can be seen to vary from 1·5 for ammonia to 26 for acetylene. It is not hard to account for these extreme values. That for ammonia is due to the fact that the gas

will only just burn in air, whilst the high value for acetylene appears to be largely due to the endothermic nature of this compound, which enables mixtures very rich in acetylene to propagate flame. The high values for hydrogen and carbon monoxide are presumably due to the fact that no carbon monoxide can be formed in these mixtures, this reaction being one that gives out relatively little heat. Similar considerations apply when the last two columns of this table are compared. For vapours, the equality of these columns showed that for downward propagation the limits were symmetrically situated with respect to a mixture midway between that for perfect combustion and one for complete combustion to carbon monoxide and water. This is far from being the case for hydrogen, carbon monoxide, or acetylene.

A comparison of the calorific values of the various limit mixtures and an examination of the theoretical flame temperatures attained at the limit for the different gases lead to precisely the same conclusion. In both cases, the variations are very much greater than for the vapours previously examined, the figures for hydrogen being always very different from those for any other gas. The theoretical flame temperature attained by hydrogen for upward propagation at the lower limit is only 360°, whilst its ignition temperature is over 500° (Dixon and Coward, J., 1909, **95**, 514).

A comparison of the results obtained for the different members of the paraffin and olefine series examined is not without interest. In general, the members of the same series behave very similarly, and the results allow of little doubt but that propane and butane would behave in much the same way as ethane and pentane. In several respects, however, the first members of the series appear to be anomalous. Thus the ratio of the upper to the lower limit for downward propagation is very high for ethylene, but low for methane. Precisely the same result is found when the ratio of the upper limit for upward propagation is compared with that for downward for these gases. The difference is so marked that for methane the upper limit for upward propagation appears to have much the same value as that for ethane. The calorific values for the lower-limit mixtures of the six paraffins and olefines and of carbon monoxide differ only by about 10%. The mean value found is lower than that previously found for vapours, and it is noteworthy that the mean value for the olefines examined is about 6% lower than that for the paraffins. That found for acetylene is, of course, considerably lower still. We thus see that to enable propagation to take place at the lower limit for the paraffins examined, the theoretical temperature attained must be greater than for one of the olefines, and considerably greater than is necessary for an acetylene–air mixture.

It is known that combination starts at a lower temperature in acetylene–air than in ethylene–air, whilst still higher temperatures are necessary to bring about the combination of methane and air. This can hardly be taken to explain satisfactorily the order found, however, as ethyl ether, acetaldehyde, and methane do not differ greatly in the theoretical temperatures needed to give propagation, although their ease of oxidation at low temperatures differs notably. Pending further work, it may be suggested that the differences mentioned are connected with the unsaturated nature of acetylene and the olefines. This might be expected to affect the rapidity with which they picked up oxygen atoms, and it is worthy of note that as far as combustible atoms alone were concerned, all the vapours used for the former work except benzene and toluene could be regarded as saturated compounds. These aromatic compounds can hardly be regarded as important exceptions, as with respect to oxidation they normally behave much as if they were saturated compounds. This provides some explanation of the uniformity of calorific value obtained for all but one of the vapours examined, as almost all the bonds to be ruptured consisted of single bonds between carbon atoms, or between one carbon and one hydrogen atom. In these circumstances, it is easy to understand why the calorific value is high for ammonia–air limit mixtures, and about twice the normal value for cyanogen–air, according to some of the author's (unpublished) results.

## Experimental.

Carbon monoxide, prepared by the dehydration of formic acid, was purified by passage through a solution of sodium hydroxide. The hydrogen was prepared by the electrolysis of barium hydroxide solution, any oxygen present being removed by passage over heated platinised asbestos. Hydrogen sulphide was prepared by the regulated action of water on aluminium sulphide, the gas used for confirmatory purposes being obtained by the action of dilute acid on pure calcium sulphide.

Methane was prepared by the purification by liquefaction and fractionation of selected cylinders of almost pure gas filled at a blower in South Wales. Ethane was procured by the action of ice-cold water on zinc ethyl, and was then purified in the same manner as methane. The pentane used was bought as pure *n*-pentane and was successively treated with concentrated sulphuric acid, distilled water, strong potassium hydroxide solution, and distilled water. It was then dried over calcium chloride and fractionated from phosphoric oxide, the liquid collected distilling between 36·5° and 37°.

The ethylene was prepared by Newth's method (J., 1901, **79**, 901), cooled in a vessel immersed in a freezing mixture, passed through a small quantity of concentrated sulphuric acid, and kept over a large volume of water for several days before use. The propylene was prepared by passing the vapour of *iso*propyl alcohol over heated pumice impregnated with phosphoric acid, the product being purified in the same way as the ethylene. The butylene was prepared from *n*-butyl alcohol by the method used for propylene, and after water cooling and washing was condensed in a freezing mixture. The liquid obtained was twice fractionated and was stored in a sulphur dioxide syphon under pressure. The acetylene used was procured from gas cylinders in which a gas of over 98% purity had been compressed without acetone. This was further purified by conversion into the acetylide.

All the gases used were of a high degree of purity, as was sufficiently evidenced by careful analyses.

The limit determinations were carried out in glass tubes 1·5 metres long and 2·5, 5·0, or 7·5 cm. in diameter. The primary source of ignition was always the spark from the secondary of a Sanax Intensified Coil, but in certain cases it was found necessary to utilise this to ignite a milligram or so of guncotton yarn, which then ignited the gas. The spark was produced at a glass-insulated brass wire electrode which was introduced through one of the two stopcocks of the limit tube just before ignition. As all trials were made with the tube closed, the end of the tube through which the electrode projected was then sealed with plasticine. A mixture was not considered to propagate flame unless the flame reached the end of the tube away from the electrode.

The mixtures were made up by volume in the tubes in which they were to be used. The measuring vessels were water-jacketed, and were easily read to 0·05 c.c. The accuracy of this method of making up the mixtures was checked by making frequent analyses. The results of such analyses were uniformly satisfactory. Each of the limit tubes contained a few c.c. of small beads, so that as tubes were shaken for ½ hour after the introduction of a gas mixture, thorough mixing of the constituent gases was ensured. With the exception of the upper-limit mixtures containing carbon monoxide, all the mixtures used contained 1% of water vapour. In the case of these carbon monoxide mixtures it was found more convenient to use 2% of moisture. An accuracy of 1% on the inflammable gas used was aimed at in the limit determinations, and all the values obtained were confirmed to this accuracy, using a different batch of the purified combustible.

*Summary.*

Limits for the propagation of flame in mixtures with air of ten combustible gases have been determined at the ordinary temperature in glass tubes up to 7·5 cm. in diameter for upward, horizontal, and downward propagation.

The lower-limit results showed that the cooling effect of the glass walls appears to be inappreciable in 7·5 cm. tubes. The upper-limit results determined in 7·5 cm. tubes sometimes differed considerably from those determined in 5·0 cm. tubes, a difference presumably to be ascribed to convection. For acetylene, these differences were very large for downward propagation, but this is probably due to a different cause.

For carbon monoxide and all the hydrocarbons examined except acetylene, it is possible to calculate the lower limit to a reasonable approximation from the calorific value of the gas concerned, and in several cases to get a rough value for the upper limit. The limit results for gases are considerably less regular than those of the vapours previously examined. It is suggested that this and certain differences between values for various gases may be accounted for by the type of bond to be ruptured when the gas or vapour burns.

I desire to express my thanks to Messrs. Nobel Industries Ltd., and particularly to Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES, ARDEER. [*Received, August 20th*, 1924.]

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## CCCXXVI.—*The Resolution of* dl-*Diphenylpropylenediamine and* dl-1 : 4-*Diphenyl*-2-*methylpiperazine.*

By FREDERIC BARRY KIPPING and WILLIAM JACKSON POPE.

CERTAIN obscurities have been noted in connexion with the stereoisomerism of the alkylpiperazines, as, for instance, that the *cis*-2 : 5-dimethylpiperazine seems not to be formed by the ordinary methods (Pope and Read, J., 1912, **101**, 2325; 1914, **105**, 219).

It is therefore desirable that a further stereochemical study should be made of the alkylpiperazines and related bases, and in the present paper the preparation of the optically active diphenylpropylenediamines and 1 : 4-diphenyl-2-methylpiperazines is described.

*Resolution of* dl-*Diphenylpropylenediamine,*

$$NHPh{\cdot}CH_2{\cdot}CHMe{\cdot}NHPh.$$

—The externally compensated compound was obtained as an oil

by Trapesonzjanz (*Ber.*, 1892, **25**, 3271) from aniline and propylene dibromide; we find that inoculation with a trace of the solid *l*-compound causes the oil to crystallise slowly to a mass of small needles; after drying on porous earthenware, the base melts at 28—29°. On evaporating an alcoholic solution of equivalent quantities of the racemic base and *d*-camphor-β-sulphonic acid, an oily salt results which crystallises on addition of acetone. After filtration and washing with acetone, the salt is crystallised several times from a mixture of acetone and alcohol and is thus obtained in colourless needles, m. p. 173°; it is very soluble in hot alcohol and moderately so in water, acetone, or ethyl acetate. This salt proves to be the l-*diphenylpropylenediamine* d-*camphor*-β-*sulphonate*, $C_{15}H_{18}N_2,2C_{10}H_{16}O_4S$, and it would seem that the salt of the *d*-base does not crystallise, as about 30% of the salt is obtained free from the *d*-base (Found: C = 60·5; H = 7·1. $C_{35}H_{50}O_8N_2S_2$ requires C = 60·9; H = 7·2%). 0·1990, made up to 20 c.c. with alcohol, gave $\alpha_{Hg} = +0{\cdot}452°$ ($l = 2$); whence $[\alpha]^{15°}_{Hg} = +22{\cdot}7°$.*

l- *and* d-*Diphenylpropylenediamine*.—On treating the above salt with aqueous sodium hydroxide, extracting with ether, drying and evaporating the ethereal solution, the *l*-base is obtained in colourless plates, m. p. 44—45°, which are very soluble in the usual organic solvents. To ensure its purity, the *l*-base was reconverted into the *d*-camphor-β-sulphonate and the salt twice recrystallised; the base recovered from the salt maintained its rotatory power unchanged (Found: C = 79·8; H = 7·9. $C_{15}H_{18}N_2$ requires C = 79·7; H = 8·0%). 0·4581, made up to 25 c.c. with alcohol, gave $\alpha_{Hg} = -0{\cdot}868°$ ($l = 2$); whence $[\alpha]^{20°}_{Hg} = -23{\cdot}7°$. 2·8971, under similar conditions, gave $\alpha_{Hg} = -3{\cdot}453°$; whence $[\alpha]^{20°}_{Hg} = -17{\cdot}88°$.

The crude *d*-base separated from the residues of the foregoing preparation was converted into the l-*camphor*-β-*sulphonate*, and the salt purified by crystallisation from a mixture of acetone and alcohol. The d-*base* prepared from this salt, like its optical antipode, melted at 44—45°; the following rotatory power determinations were made. 0·4582, made up to 25 c.c. with alcohol, gave $\alpha_{Hg} = +0{\cdot}896°$ ($l = 2$); whence $[\alpha]^{20°}_{Hg} = +24{\cdot}4°$; 2·9137, under similar conditions, gave $\alpha_{Hg} = +3{\cdot}570°$, whence $[\alpha]^{20°}_{Hg} = +18{\cdot}38°$. It will be noted that the rotatory powers of these enantiomorphously related bases diminish considerably as the concentration increases.

d- *and* l-*Diacetyldiphenylpropylenediamine*.—The externally compensated compound was prepared by Trapesonzjanz and melts at

* Throughout this paper the rotatory powers given are for the green mercury line.

147°; the diacetyl derivatives of the optically active bases are obtained by boiling for a few minutes with acetic anhydride and form colourless crystals, m. p. 101—102° (Found: for *d*-compound, C = 73·7; H = 7·1. $C_{19}H_{22}O_2N_2$ requires C = 73·6; H = 7·1%). 0·1578 of the *d*-compound, made up to 25 c.c. with alcohol, gave $\alpha_{Hg} = +1·79°$ ($l = 2$); whence $[\alpha]^{20°}_{Hg} = +142°$. 0·1577 of the *l*-compound similarly gave $\alpha_{Hg} = -1·73°$ and $[\alpha]^{20°}_{Hg} = -138°$.

d- *and* l-*Dibenzoyldiphenylpropylenediamine*.—The externally compensated substance melts at 140—141° (Trapesonzjanz gives 136—137°) and it and its optically active components are obtained by boiling the corresponding bases with benzoyl chloride in pyridine solution. The d- and l-*isomerides* crystallise from alcohol in short, stout needles, m. p. 144°, and are readily soluble in alcohol, chloroform, benzene, or carbon disulphide (Found: C = 79·7; H = 6·0. $C_{29}H_{26}O_2N_2$ requires C = 80·2; H = 6·0%). 0·2541 of the *l*-benzoyl derivative, made up to 25 c.c. with alcohol, gave $\alpha_{Hg} = -4·428°$ ($l = 2$) at 20°; 0·2544 of the *d*-isomeride similarly gave $\alpha_{Hg} = +4·512°$; whence the respective values for $[\alpha]^{20°}_{Hg}$ are given as −218° and + 221°.

dl-*Benzenesulphonyldiphenylpropylenediamine*,

$$C_6H_5{\cdot}SO_2{\cdot}NPh{\cdot}CH_2{\cdot}CHMe{\cdot}NHPh.$$

—On heating the racemic base (2·3 g.) with benzenesulphonyl chloride (3·5 g.) and potassium carbonate (2 g.) in alcoholic solution, and filtering hot, a filtrate results from which the hydrochloride of the above base separates on cooling. The *hydrochloride* is practically insoluble in water and is obtained in small, colourless crystals, m. p. 212—213°, on crystallisation from alcohol (Found: C = 62·4; H = 5·7. $C_{21}H_{22}O_2N_2S,HCl$ requires C = 62·6; H = 5·7%). The base is obtained by treating the salt with aqueous ammonia and forms colourless crystals, m. p. 151—152°, on crystallisation from alcohol (Found: C = 69·0; H = 6·0. $C_{21}H_{22}O_2N_2S$ requires C = 68·9; H = 6·0%).

d- *and* l-*Benzenesulphonyldiphenylpropylenediamines*.—The *hydrochlorides* of these bases form small, colourless crystals, m. p. 228°, and the free bases crystallise from alcohol in colourless needles, m. p. 161—162°. 0·3225 of the *d*-base, made up to 25 c.c. with acetone, gave $\alpha_{Hg} = -1·022°$ ($l = 2$) at 20°; 0·3231 of the *l*-base similarly gave $\alpha_{Hg} = +1·006°$; whence the respective values for $[\alpha]^{20°}_{Hg}$ are given as −39·6° and + 38·9°. It will be noted that whilst dibenzoyl- and diacetyl-diphenylpropylenediamines have the same sign of rotatory power as the parent bases, the monobenzenesulphonyl derivatives have the opposite sign; it has not yet been determined to which of the diamine nitrogen atoms the benzenesulphonyl group is attached.

dl-, d-, *and* l-1 : 4-*Diphenyl-2-methylpiperazines.*

$$N{\cdot}Ph\langle\begin{matrix}CHMe{\cdot}CH_2\\CH_2{-}CH_2\end{matrix}\rangle NPh.$$

—The externally compensated base, obtained by the method of Trapesonzjanz, melts at 102—103°. The optically active bases were similarly prepared from *d*- and *l*-diphenylpropylendiamines as colourless crystals, m. p. 96° (Found: C = 80·9; H = 7·8. $C_{17}H_{20}N_2$ requires C = 81·0; H = 7·9%). These piperazines are of opposite sign of rotation to the diphenylpropylenediamines from which they are made. 1·0767 of the *l*-base, made up to 25 c.c. with chloroform, gave $\alpha_{Hg} = +2{\cdot}108°$ ($l = 2$); 1·0432 of the *d*-base similarly gave $\alpha_{Hg} = -2{\cdot}106°$; whence the respective values for $[\alpha]^{20°}_{Hg}$ are given as + 24·5° and −25·2°.

It is interesting to note that the optical activity of the original diphenylpropylenediamine persists, although the sign is reversed, after the somewhat drastic treatment involved in the production of the piperazine; it thus became important to ascertain whether any racemisation attends the formation of the piperazine and for this purpose the externally compensated piperazine was resolved by treatment with *d*-camphor-β-sulphonic acid.

The *dl*-base and the *d*-acid were separately dissolved in hot acetone in equivalent proportion and the solutions mixed; on cooling, a colourless, crystalline salt separated which was recrystallised from a mixture of acetone and alcohol until its rotatory power was constant. The salt thus obtained proves to be the l-1 : 4-*diphenyl-2-methylpiperazine* d-*camphor-β-sulphonate*,

$$C_{17}H_{20}N_2{,}2C_{10}H_{16}O_4S;$$

it melts at 175° and is hydrolysed by water. 0·5324 of the salt, made up to 25 c.c. with alcohol, gave $\alpha_{Hg} = +1{\cdot}40°$ ($l = 2$); whence $[\alpha]^{20°}_{Hg} = +32{\cdot}9°$ (Found: C = 61·8; H = 7·1. $C_{37}H_{52}O_8N_2S_2$ requires C = 62·0; H = 7·26%).

The base was liberated by treatment with ammonia and after crystallisation from alcohol melted at 95—96°. 0·8273, made up to 25 c.c. with chloroform, gave $\alpha_{Hg} = +1{\cdot}65°$ ($l = 2$); whence $[\alpha]^{20°}_{Hg} = +24{\cdot}95°$. The practical identity of this value with those given by the bases prepared from the optically active diphenylpropylenediamines proves that no racemisation occurs during the formation of the piperazines from the latter bases.

The *d*- and *l*-1 : 4-diphenyl-2-methylpiperazines are the first optically active piperazines which have been prepared.

THE CHEMICAL LABORATORY,
UNIVERSITY OF CAMBRIDGE.

[*Received, August* 21*st*, 1924.

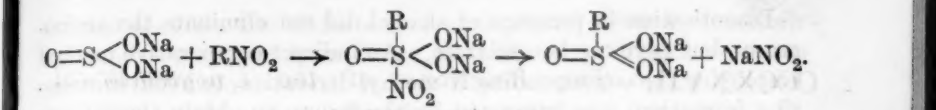
# CCCXXVII.—*The Reactions of the Unsymmetrical Trinitrotoluenes.*

By O. L. Brady, S. W. Hewetson, and L. Klein.

A process for the purification of crude trinitrotoluene was employed in France and later in this country which consisted in washing with an aqueous solution of sodium sulphite; by this means the 2 : 3 : 4- and 3 : 4 : 6-trinitrotoluenes present in small quantities in the crude 2 : 4 : 6-trinitrotoluene were dissolved (Ministry of Munitions, Technical Records of Explosives Supply, No. 2, p. 23). Muraour (*Bull. Soc. chim.*, 1924, [iv], **35**, 367), describing this process, states that the soluble compounds are sodium dinitrotoluenesulphonates, but does not seem to have isolated them in a pure state. These compounds were investigated by us in 1922—23, but publication was delayed pending further work. In view, however, of Muraour's paper, we think it desirable to put our results on record, as there is no immediate prospect of continuing this investigation.

The action of sodium sulphite on a polynitrobenzenoid compound was studied by Laubenheimer (*Ber.*, 1882, **15**, 597), who found that 3 : 4-dinitrochlorobenzene, on treatment with an aqueous solution of sodium sulphite, gave sodium 4-nitrochlorobenzene-3-sulphonate. We have now found that this reaction is apparently general with compounds containing a mobile nitro-group, and the unsymmetrical trinitrotoluenes are readily acted upon by aqueous sodium sulphite at room temperature; for example, 2 : 3 : 4-trinitrotoluene gives sodium 2 : 4-dinitrotoluene-3-sulphonate, whilst 3 : 4 : 6-, 3 : 4 : 5-, and 2 : 3 : 5-trinitrotoluenes give respectively sodium 4 : 6-dinitrotoluene-3-sulphonate, 3 : 5-dinitrotoluene-4-sulphonate, and 3 : 5-dinitrotoluene-2-sulphonate.

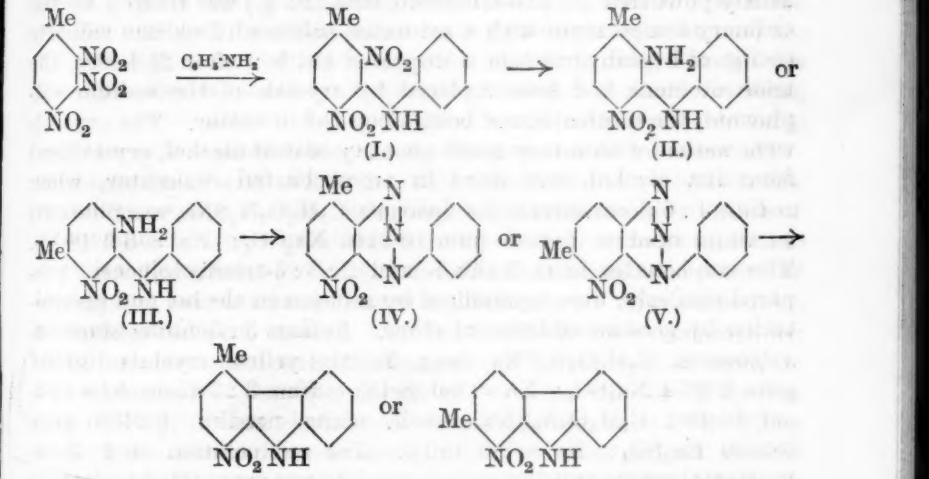
The sodium dinitrotoluenesulphonates are crystalline compounds, soluble in such solvents as water and alcohol, but insoluble in ether, benzene, etc. They deflagrate violently on heating. They are not readily acted on by aqueous or alcoholic ammonia (compare Muraour, *loc. cit.*), but are decomposed by methylamine, giving the known dinitromethyltoluidines, by which means the position of the sulphonic acid group can be determined. All attempts to remove the sulpho-group by hydrolysis, with production of the dinitrotoluenes, have been unsuccessful. Only one sodium atom in the sodium sulphite is replaceable and this together with the formation of a sulphonate seems to afford evidence for the unsymmetrical structure of the alkali sulphites. On the other hand, the reaction might be regarded as an additive one, thus :—



Sodium acetate in concentrated aqueous solution behaves towards the unsymmetrical trinitrotoluenes as a mild alkali, giving the dinitrocresols with less of the amorphous compounds formed by the action of stronger alkalis.

2 : 3 : 6-Trinitrotoluene has been partly investigated (Brady, J., 1922, **121**, 328) and is abnormal in its reactions.

An attempt has been made to prepare nitromethylcarbazoles, starting, for example, from 2 : 3 : 4-trinitrotoluene, by the following series of reactions (compare Graebe and Ullmann, *Annalen*, 1896, **291**, 16) :



The last stage of this synthesis, however, failed, the nitrophenylmethylbenztriazole being remarkably stable and not losing nitrogen on heating. Delétra and Ullmann (*Arch. Sci. phys. nat.*, 1904, [v], **17**, 78), who experienced a similar difficulty with 5-nitro-1-phenyl-1 : 2 : 3-benztriazole, found that after reduction of the nitro-group the compound behaved normally. Ammonium sulphide did not reduce the nitrophenylmethylbenztriazole, whilst stannous chloride, the reagent used by Delétra and Ullmann, apparently reduced the azimino-group. In (I), either of the nitro-groups may be reduced, giving (II) or (III). The decision between the two would have been possible had the preparation of the carbazole been successful; when this failed, other methods of orientation were tried, but without success.

Diazotisation in presence of alcohol did not eliminate the amino-group, but gave the benztriazole. An indirect comparative method employing the corresponding *N*-methyl derivative, to avoid azimino-ring formation, was frustrated by the failure to obtain the 2-nitro-*N* : 5-dimethyldiphenylamine, needed for comparison, by the action of methylaniline on 3 : 4-dinitrotoluene. An attempt to synthesise one of the alternative compounds by the action of aniline on 3-chloro-2-nitro-*p*-toluidine was unsuccessful, no reaction occurring even at the temperature of boiling aniline.

The action of a number of amines on the unsymmetrical trinitrotoluenes has also been investigated.

## Experimental.

*Action of Sodium Sulphite on the Unsymmetrical Trinitrotoluenes.*—Finely powdered 3 : 4 : 6-trinitrotoluene (2·2 g.) was treated at the ordinary temperature with a saturated solution of sodium sulphite (2·5 g. of heptahydrate) in a stoppered bottle; after 24 hours, the trinitrotoluene had been replaced by crystals of the sodium sulphonate, the mother-liquor being deep red in colour. The crystals were washed with a very small quantity of cold alcohol, crystallised from hot alcohol, and dried in an evacuated desiccator, when *sodium* 4 : 6-*dinitrotoluene*-3-*sulphonate*, $C_7H_5O_7N_2SNa$, was obtained as white needles [0·4548 gave 0·1145 $Na_2SO_4$; Na = 8·2 (8·1)]. The sulphonates from 3 : 4 : 5- and 2 : 3 : 5-trinitrotoluenes, prepared similarly, were crystallised by solution in alcohol and precipitation by gradual addition of ether. *Sodium* 3 : 5-*dinitrotoluene*-4-*sulphonate*, $C_7H_5O_7N_2SNa$, long, faintly yellow crystals [0·1511 gave 0·0374 $Na_2SO_4$; Na = 8·0 (8·1)], *sodium*-3 : 5-*dinitrotoluene*-2-*sulphonate*, $C_7H_5O_7N_2SNa$, small, white needles [0·2400 gave 0·0590 $Na_2SO_4$; Na = 8·0 (8·1)]. The red solution of 2 : 3 : 4-trinitrotoluene in aqueous sodium sulphite was evaporated to dryness on the water-bath, the residue extracted with hot absolute alcohol, and the sulphonate precipitated with ether; most of the red material was insoluble in alcohol. Redissolving in alcohol and reprecipitating gave *sodium* 2 : 4-*dinitrotoluene*-3-*sulphonate*, $C_7H_5O_7N_2SNa$, as a faintly pink, crystalline powder [0·5886 gave 0·1466 $Na_2SO_4$; Na = 8·1(8·1)]. The yields of the purified compounds were small, except in the cases of sodium 3 : 5-dinitrotoluene-2- and 2 : 4-dinitrotoluene-3-sulphonates, owing to their solubility.

*Action of Sodium Acetate on Unsymmetrical Trinitrotoluenes.*—A mixture of the trinitrotoluene (5 g.) and crystallised sodium acetate (50 g.) was heated on the water-bath until the latter melted and then on a sand-bath under reflux for 6—7 hours. The homogeneous solution was cooled, just sufficient water added to dissolve the

sodium acetate, the dinitrocresol precipitated with hydrochloric acid and crystallised from dilute alcohol. 2 : 3 : 4-Trinitrotoluene gave 2 : 4-dinitro-*m*-cresol, m. p. 100·5°, in 50% yield (Found, N = 13·9. Calc., 14·1). Nietzki and Ruppert (*Ber.*, 1890, **23**, 3479) obtained this compound from aminocresotinic acid; Will (*Ber.*, 1914, **47**, 712), prepared it from the trinitrotoluene, but supplies neither directions nor analysis. 3 : 4 : 6-Trinitrotoluene gave 4 : 6-dinitro-*m*-cresol, m. p. 73°, in poor yield, a considerable amount of tarry matter being formed during the heating (Found, N = 14·0). Will (*loc. cit.*) obtained it from the trinitrotoluene and gives m. p. 74°; Gibbs and Robertson (J., 1914, **105**, 1889), who obtained it by the nitration of 4-nitro-*m*-cresol, give 60°, whilst Borsche (*Ber.*, 1917, **50**, 1342, 1350), who obtained it by the action of sodium acetate and acetamide at 180° on 3-chloro-4 : 6-dinitrotoluene, gives m. p. 63—65°. We consider 73—74° the most correct. 3 : 4 : 5-Trinitrotoluene gave 3 : 5-dinitro-*p*-cresol, m. p. 85° (Found, N = 14·2) in poor yield, and 2 : 3 : 5-trinitrotoluene gave 3 : 5-dinitro-*o*-cresol, m. p. 85° (Found, N = 14·1), in 60% yield.

*Action of Aromatic Amines on the Unsymmetrical Trinitrotoluenes.* (Compare Ryan and O'Riordan, *Proc. Roy. Irish Acad.*, 1918, **34**, 175).—The trinitrotoluene (4 g.) in boiling alcohol (80 c.c.) was mixed with a solution of the toluidine (4 g.) or naphthylamine (5·7 g.) in hot alcohol (20 c.c.), warmed for a minute, and allowed to cool slowly, when the compound crystallised; it was purified by crystallisation from alcohol. 2 : 3 : 4-Trinitrotoluene with *m*-toluidine or with β-naphthylamine gave 2 : 6-*dinitro*-3 : 3′-*dimethyldiphenylamine*, $C_{14}H_{13}O_4N_3$, brick red, m. p. 110° [0·1902 gave 25·6 c.c. $N_2$ (21°, 717 mm.); N = 14·8 (14·6)], and 2 : 6-*dinitro*-3-*methylphenyl*-β-*naphthylamine*, $C_{17}H_{13}O_4N_3$, ruby red, m. p. 166° [0·2179 gave 24·2 c.c. $N_2$ (24°, 747 mm.); N = 12·6 (13·0)]. 3 : 4 : 6-Trinitrotoluene with *m*-toluidine, *o*-toluidine, or with α- or β-naphthylamine gave 4 : 6-*dinitro*-3 : 3′-*dimethyldiphenylamine*, $C_{14}H_{13}O_4N_3$, orange, m. p. 135° [0·1957 gave 25·0 c.c. $N_2$ (17°, 749 mm.); N = 14·9 (14·6)], 4 : 6-*dinitro*-3 : 6′-*dimethyldiphenylamine*, $C_{14}H_{13}O_4N_3$, brownish-red, m. p. 99° [0·1685 gave 22·0 c.c. $N_2$ (21°, 734 mm.); N = 14·7 (14·6)], 4 : 6-*dinitro*-3-*methylphenyl*-α-*naphthylamine*, $C_{17}H_{13}O_4N_3$, dark brown, m. p. 182° [0·1288 gave 15·5 c.c. $N_2$ (25°, 738 mm.); N = 13·4 (13·0)], and 4 : 6-*dinitro*-3-*methylphenyl*-β-*naphthylamine*, $C_{17}H_{13}O_4N_3$, orange (from acetone), m. p. 211° [0·1446 gave 17·1 c.c. $N_2$ (23°, 736 mm.); N = 13·2 (13·0)]. 2 : 3 : 5-Trinitrotoluene with *o*-toluidine gave 4 : 6-*dinitro*-2 : 2′-*dimethyldiphenylamine*, tangerine-red, m. p. 109° [0·1361 gave 17·2 c.c. $N_2$ (20·6°, 742 mm.); N = 14·5 (14·6)].

2 : 4 : 6 : 2′ : 4′ : 6′-*Hexanitro*-3 : 3′-*dimethyldiphenylamine*.—4 : 6-Dinitro-3 : 3′-dimethyldiphenylamine was dissolved in excess of nitric acid (*d* 1·5) in small portions, the solution warmed cautiously on the water-bath until no more red fumes were evolved and poured into water. The precipitated hexanitro-compound, $C_{14}H_9O_{12}N_7$, crystallised from dilute alcohol in brown plates, m. p. 60° [0·1263 gave 23·4 c.c. $N_2$ (24°, 744 mm.); N = 21·0 (21·0)]. The nitration does not proceed as smoothly as that of 2 : 4-dinitrodiphenylamine and much oxidation occurs, the yield being but 20%; 2 : 6-dinitro-3 : 3′-dimethyldiphenylamine was decomposed even more completely, only a trace of the same hexanitro-compound being obtained.

6-*Nitro*-2-*amino*-3- (*or* 5-) *methyldiphenylamine* (II or III).—2 : 6-Dinitro-3-methyldiphenylamine (I) (21·5 g.), prepared from 2 : 3 : 4-trinitrotoluene (Ryan and O'Riordan, *Proc. Roy. Irish Acad.*, 1918, **34**, 175), dissolved in the minimum of hot alcohol, was heated with ammonium sulphide solution (111 g. of 15%) on the water-bath for 1 hour, and the solution then diluted with hot water until precipitation was complete; after cooling, the precipitate was washed, and extracted with successive small quantities of boiling dilute hydrochloric acid until a test-portion of the filtrate no longer gave a precipitate with ammonia. The combined filtrates were evaporated to small bulk, treated cautiously, while still hot, with concentrated ammonia until strongly alkaline, and cooled. The precipitate was crystallised 3 times from alcohol, and 6-nitro-2-amino-3- (or 5-) methyldiphenylamine, $C_{13}H_{13}O_2N_3$, obtained in golden-yellow scales, m. p. 139° [0·1354 gave 20·5 c.c. $N_2$ (21°, 740 mm.); N=17·2 (17·3)].

7-*Nitro*-1-*phenyl*-4- (or 6-)*methyl*-1 : 2 : 3-*benztriazole* (IV or V).—The above compound (12 g.), dissolved in concentrated hydrochloric acid (300 c.c.), water (300 c.c.), and glacial acetic acid (150 c.c.), cooled to 0°, was treated with a concentrated solution of sodium nitrite until excess was present. After 30 minutes, the precipitate was crystallised from alcohol, when 9 g. of the benztriazole, $C_{13}H_{10}O_2N_4$, was obtained as long, buff-coloured needles, m. p. 147° [0·1275 gave 24·4 c.c. $N_2$ (17°, 730 mm.); N = 21·8 (22·0)]. When this compound, mixed with kieselguhr, was heated, some charring took place, but most of it sublimed unchanged.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, September 8th*, 1924.]

# CCCXXVIII.—*Condensation of Diphenylformamidine with Phenols. Part II. The General Nature of the Reaction.*

By JOHN BALDWIN SHOESMITH and JOHN HALDANE.

In Part I (J., 1923, **123**, 2704), it was shown that the products formed by condensing resorcinol with diphenylformamidine yield, on hydrolysis, β-resorcylaldehyde and 4 : 6-dihydroxy*iso*phthalaldehyde. The reaction has now been extended to resorcinol monomethyl ether, guaiacol, pyrogallol, phenol, the isomeric cresols, and α- and β-naphthols. The aldehydo-group enters in the ortho-position to a hydroxyl group, and the yield of hydroxyaldehyde varies from 60% in the case of β-naphthol to 10% from phenol, although, in general, the primary condensation appears to be complete. The chief by-products are resins of a "bakelite" nature. By this means 1-hydroxy-2-naphthaldehyde is more readily obtainable than by Friedländer's process (*Ber.*, 1908, **41**, 1037).

Further, it is shown that the reaction takes place as assumed already (*loc. cit.*), the intermediate products, 2-hydroxy-1-naphthylideneaniline, $OH{\cdot}C_{10}H_6{\cdot}CH{:}NPh$, and 4 : 6-dihydroxy*iso*phthalylidenebisaniline, $C_6H_2(OH)_2(CH{:}NPh)_2$, having been isolated in the condensation of diphenylformamidine with β-naphthol and resorcinol, respectively.

## EXPERIMENTAL.

To insure constancy of temperature, the condensation flasks were immersed in vapour from a boiling liquid. To obtain a temperature between 80° and 140°, a mixture of benzene, toluene, and xylene was distilled until the temperature was reached and then the condenser was tilted back and used as a reflux. This method is especially useful when the condensation is very susceptible to slight temperature changes, as the diphenylformamidine condensations have proved to be.

*Condensations with β-Naphthol.*—A mixture of diphenylformamidine (7 g.) and β-naphthol (5 g.) was heated at 130° for 6 hours, a slight excess (16 c.c.) of 10% aqueous sodium hydroxide added, the liberated aniline distilled in steam, the solution cooled, the unchanged diphenylformamidine (0·6 g.) filtered off, and the filtrate acidified. The precipitate of β-naphthol and 2-hydroxy-1-naphthaldehyde was boiled with alcoholic aniline, the Schiff's base of the aldehyde, which separated from the cooled solution, was hydrolysed with aqueous sodium hydroxide as before, the aniline removed with steam, and the aldehyde (2·9 g.), precipitated as a yellow-

brown solid on addition of hydrochloric acid, crystallised from alcohol, separating in yellow prisms, m. p. 81°.

*Condensation with α-Naphthol.*—Diphenylformamidine (7 g.) and α-naphthol (5 g.) were heated together at 95° for 6 hours. The reaction product was hydrolysed as before. The dark green resin that appeared during the steam distillation was removed, a saturated solution of sodium chloride added to the green filtrate, the sodium salt of the aldehyde, which separated in yellow-green, leafy crystals, was washed with a saturated solution of common salt, decomposed with hydrochloric acid, and the 1-hydroxy-2-naphthaldehyde distilled in steam (yield 1·4 g., m. p. 58—59°, after crystallisation from alcohol).

*Condensation with Resorcinol Monomethyl Ether.*—This was carried out at 183—184° for 2 hours. After hydrolysis of the condensation product with sodium hydroxide and distillation of the aniline in steam, 2-hydroxy-4-methoxybenzaldehyde was extracted from the cooled, acidified solution with ether, separated from the extract with sodium bisulphite solution, and recrystallised from dilute alcohol (m. p. 41°; yield 20%).

*Condensation with Guaiacol.*—Temperature 210°; time 6 hours. 2-Hydroxy-3-methoxybenzaldehyde was isolated as in the preceding case (yield *ca.* 10%).

*Condensation with Pyrogallol.*—Temperature 110°; time 4 hours. 2 : 3 : 4-Trihydroxybenzaldehyde was separated by the bisulphite method (yield 20%).

*Condensations with the Isomeric Cresols.*—*o*-Cresol: temperature 183°; time 6 hours. The aniline was distilled in steam, the intermediate product hydrolysed as before, the liberated aniline distilled in steam, unchanged diphenylformamidine removed, the filtrate acidified with hydrochloric acid, and 2-hydroxy-3-methylbenzaldehyde isolated therefrom by distillation with steam and extraction of the distillate with ether (yield 25%).

*m*-Cresol: temperature 210°; time 6 hours. The yield of 2-hydroxy-4-methylbenzaldehyde, m. p. 59°, was *ca.* 20%.

*p*-Cresol: temperature 193°; time 6 hours. Under the best conditions, the yield of 2-hydroxy-5-methylbenzaldehyde, m. p. 56°, was only 15%.

Salicylaldehyde (yield 10%) was obtained from phenol in a similar manner. The condensation was carried out at 183° for 6 hours. Sodium bisulphite was used in order to extract the aldehyde from the ethereal solution; otherwise it was found to be contaminated with phenol. The method cannot be recommended in this case.

*Isolation of the Pure Intermediate Compounds.*—(1) 2-Hydroxy-1-naphthylideneaniline. The crude condensation product from

diphenylformamidine and β-naphthol was dissolved in warm alcohol containing a small quantity of aniline (diphenylformamidine is very soluble in such a mixture). The yellow needles of 2-hydroxy-1-naphthylideneaniline that separated from the cooled solution were almost identical with a sample prepared from 2-hydroxy-1-naphthaldehyde by Gattermann and Horlacher's method (*Ber.*, 1899, **32**, 286), and when purified by Manchot and Palmberg's method (*Annalen*, 1912, **388**, 112) melted at 92—93°.

(2) 4 : 6-Dihydroxy*iso*phthalylidenebisaniline. It has not been possible to isolate the intermediate compound from pure dry resorcinol and diphenylformamidine in a state of purity which would justify speculation as to its composition. When ordinary resorcinol was used, however, the pure intermediate 4 : 6-dihydroxy*iso*-phthalylidenebisaniline was obtained. The crude reaction product was washed free from diphenylformamidine with aniline, pressed on porous tile, and recrystallised from alcohol. It had m. p. 202—203° and was identical with the Schiff's base of 4 : 6-dihydroxy-*iso*phthalaldehyde prepared from the aldehyde as described by Tiemann and Lewy (*Ber.*, 1877, **10**, 2212; they give m. p. 199°).

Aldehydes could not be isolated from the products of reaction between diphenylformamidine and catechol, quinol, phloroglucinol, and *p*-nitrophenol. The very marked odour of phenylcarbylamine which was observed in the reaction product suggests that the reaction is essentially a decomposition of the diphenylformamidine into aniline and phenylcarbylamine: $NHPh{\cdot}CH{:}NPh \rightarrow NH_2Ph + Ph{\cdot}N{:}C$.

This decomposition also takes place when the formamidine is heated alone at 250°.

Diphenylformamidine appears to be stable in presence of resorcinol dimethyl ether or *o*-nitrophenol under all conditions.

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# CCCXXIX.—*Blue Adsorption Compounds of Iodine. Part IV.*

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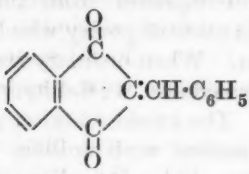
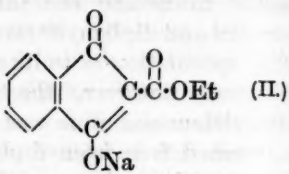
IT was shown in Part III (Barger and Starling, J., 1915, **107**, 411) that a large number of synthetic organic compounds give blue addition compounds with iodine, similar to the so-called starch

"iodide"; in the present paper, some constitutive and ionic influences on the formation of these compounds are discussed.

*Crossed Conjugated Double Bonds.*—It was shown previously (*loc. cit.*, p. 415) that some of the best examples showing the reaction are substances having crossed conjugated double bonds, such as γ-pyrone derivatives. In order further to test the influence of this grouping we have examined a number of derivatives of 1 : 3-diketohydrindene, for instance, 2-benzylidene-1 : 3-indanedione (I) (Nathanson, *Ber.*, 1893, **26**, 2578) and the corresponding *o*-hydr-

(I.) 

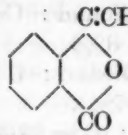
(II.) 

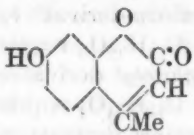
oxybenzylidene derivative (Kostanecki and Laczkowski, *Ber.*, 1897, **30**, 2138). Contrary to our expectation, neither of these furnishes a blue addition compound; 1 : 3-diketohydrindene and its 2-methyl derivative do not either, but the sodium derivative of ethyl 1 : 3-diketohydrindenecarboxylate (Wislicenus and Kötzle, *Annalen*, 1888, **246**, 349; 1889, **252**, 72) gives in aqueous solution on addition of potassium tri-iodide a blue precipitate, which disappears on warming and reappears on cooling; the concentration of the iodine after mixing should be at least $N/200$. The corresponding free ester does not give a blue compound. Possibly the sodium derivative, unlike the free ester, has the constitution (II). The disodium salt of 1 : 3-diketohydrindenecarboxylic acid (Gabriel and Neumann, *Ber.*, 1893, **26**, 953) behaves like the monosodium salt, but the sodium derivative of 2-propionyl-1 : 3-diketohydrindene (Schwerin, *Ber.*, 1894, **27**, 104) does not add iodine.

It seems from these examples that there is a great divergence among closely allied compounds and that the occurrence of a crossed conjugated double bond is not enough to ensure adsorption of iodine. A further example of this divergence is shown by *o*-hydroxybenzylideneacetophenone (best prepared according to Borsche, *Ber.*, 1900, **33**, 1327) and its benzoyl derivative. A solution of the former in the minimum quantity of alkali, when mixed with potassium tri-iodide and acidified, forms a blue compound up to a dilution of $N/2500$ iodine; the latter does not, even when $N/100$ iodine is used to precipitate it from alcoholic solution.

*The Bridge Oxygen Atom.*—Since, in Part III, α- and γ-pyrones were found to be among the best adsorbents of iodine, we examined a further group of substances possessing a bridge oxygen atom,

*viz.*, the phthalides. Ethylidenephthalide (Gabriel, *Ber.*, 1886, **19**, 838) in alcoholic solution gives with *N*/50-aqueous iodine a

(III.) 

(IV.)

brown, colloidal solution, from which a greenish-blue, amorphous precipitate gradually separates, not at all characteristic. Benzylidenephthalide (III), on the other hand, forms relatively stable colloidal solutions, even when very dilute alcoholic solutions (*M*/250,000) are diluted with water. These colloidal solutions turn blue on the addition of iodine, in much the same way as starch solutions do.

When the molecular weight is increased still further, as in ethylenediphthalide (Kaufmann, *Ber.*, 1897, **30**, 386), fluorenephthalide (Wislicenus and Neber, *Annalen*, 1919, **418**, 274), and diphenylphthalide (Friedel and Crafts, *Ann. Chim. Phys.*, 1884, [vi], **1**, 523), the substance in each case separates out colourless, when its solution in an organic solvent (alcohol, glacial acetic acid) is mixed with potassium tri-iodide. In these cases, the similarity of constitution again fails to bring about similarity of behaviour towards iodine. The main influence seems to be of a physical nature; the benzylidene compound alone forms colloidal solutions, and it alone resembles starch in its behaviour towards iodine. The capacity to form colloidal solutions must in the end depend on chemical constitution, but the connexion is quite obscure; of course the formation of a colloidal solution is in itself insufficient to induce iodine adsorption; there must also be some kind of residual valency. This point has recently been insisted on by Bergmann (*Ber.*, 1924, **57**, [*B*], 755), who has described some blue, crystalline iodine addition-compounds of *cyclo*-acetals. He attributes their formation to the bridge oxygen atom, which he also supposes present in starch; this would connect starch with the α- and γ-pyrones, phthalides, etc. This does not, however, exhaust the list of substances capable of adding iodine.

*Derivatives of 7-hydroxy-4-methylcoumarin.*—Since the examples given in the two previous sections do not indicate a close connexion between chemical constitution and power of adsorbing iodine, we examined a series of acyl and aryl derivatives of 7-hydroxy-4-methylcoumarin (IV). It was shown in Part III (p. 417) that this substance does not itself add iodine, nor does its acetyl derivative; the benzoyl compound behaves in a remarkable manner, forming deep blue colloidal solutions with only very little iodine,

and having a great power for forming a gel. Using Einhorn's method, we prepared the following compounds :

1. *Carbethoxy*-derivative, m. p., 99—100° (Found : C = 62·5; H = 4·9. $C_{13}H_{12}O_5$ requires C = 62·9; H = 4·8%).

2. *Phenylacetyl* derivative, m. p. 102—103° (Found : C = 74·3; H = 4·6. $C_{18}H_{14}O_4$ requires C = 72·5; H = 4·7%).

3. *Cinnamoyl* derivative, m. p. 154° (Found : C = 74·3; H = 4·6. $C_{19}H_{14}O_4$ requires C = 74·5; H = 4·6%).

4. β-*Naphthoyl* derivative, m. p. 179—180° (Found : C = 76·2; H = 4·1. $C_{21}H_{14}O_4$ requires C = 76·4; H = 4·1%).

5. o-*Chlorobenzoyl* derivative, m. p. 155—156° (Found : Cl = 11·3. $C_{17}H_{11}O_4Cl$ requires Cl = 11·3%).

6. m-*Nitrobenzoyl* derivative, m. p. = 210—211° (Found : N = 4·2. $C_{17}H_{11}O_6N$ requires N = 4·3%).

7. p-*Nitrobenzoyl* derivative, m. p. = 143° (Found : N = 4·3. $C_{17}H_{11}O_6N$ requires N = 4·3%).

8. *Phenylcarbimido*-derivative, m. p. 155—156° (Found : N = 4·9. $C_{17}H_{13}O_4N$ requires N = 4·7%).

All these eight substances gave blue additive compounds with iodine, but at very different concentrations. Expressing the final iodine concentrations by the reciprocal of normality (*i.e.*, number of litres containing 1 gram-atom of iodine), they were respectively : 40, 100, 500, 1000, 4000, 5000, 3000, 10. No. 2 formed blue, and No. 8 bluish-black, crystals ; the others gave apparently amorphous adsorption compounds, which, like the benzoyl derivative previously described, lost iodine on keeping and were in most cases transformed to colourless crystals of the organic compound employed. None of the eight substances forms a blue sol quite so readily as the benzoyl derivative, which does so even with *N*/10,000-iodine. It will be seen that the *o*-chlorobenzoyl and the *m*- and *p*-nitrobenzoyl approached most nearly to the benzoyl compound in adsorptive power, as they do in chemical constitution; the β-naphthoyl derivative comes next. The phenylcarbimido-derivative is of a rather different type on account of the nitrogen atom, so that with *N*/100-iodine it gives a brown addition compound, resembling the periodides of the alkaloids and of other bases.

Since, as has been pointed out in Part III, the adsorption of iodine is often favoured by the addition of acid, we originally expected that the adsorption power of the benzoyl derivative would be enhanced by the introduction of negative substituents, like the chlorine atom or the nitro-group, but this enhancement does not occur. The great adsorptive power of the benzoyl derivative seems due to the capacity of that substance to form a sol, when its alcoholic solution is poured into water. The other derivatives were more

apt to separate in flakes or in crystals under these conditions. In this group we therefore arrive at a similar conclusion to that reached in the previous section, dealing with phthalides.

*Effect of the Concentration of Hydrogen- and other Ions on Adsorption.*—In order to test the effect of the hydrogen-ion concentration, an alcoholic solution of the substance to be investigated was poured on to an aqueous solution containing disodium hydrogen phosphate and phosphoric acid in various proportions, together with constant amounts of potassium iodide and iodine. With care, this could be done in a test-tube without much mixing taking place. A series of tubes so prepared could then be shaken up simultaneously and the time of appearance of the blue colour noted. By separate experiments we ascertained that wide variations in the phosphate-ion concentration affected neither the rapidity with which the blue colour appeared, nor its intensity. As an example, the case of benzoyl-β-methylumbelliferone may be given: 2 c.c. 0·14% alcoholic solution of this compound + 2 c.c. of $N/1000$-iodine + 5 c.c. of buffer solution; final iodine concentration therefore $N/4500$. Here and in the corresponding case of the *o*-chlorobenzoyl derivative the optimum $p_H$ was 1·2—1·5. With α-naphthaflavone, adsorption is likewise favoured in acid solution: with $p_H > 4$, the blue colour only appeared on keeping, at $p_H$ 1·5 it was produced at once. The influence of hydrogen-ion concentration is shown in another way by the peculiar behaviour of indenoflavone, which is more sensitive to iodine than starch itself; in dilutions up to 10,000, the colour is blue, at greater dilution it is violet, and at 40,000—60,000 it is pink (Part III, p. 422). We now find that the pink colour is produced in solutions much more concentrated than $N/10,000$, if they are slightly alkaline. Thus, with 0·2 c.c. of 0·05% indenoflavone, 1 c.c. of $N/1000$-iodine, and 5 c.c. of buffer solution, the colour of the adsorption compound was pink at $p_H = 10$, violet at $p_H = 8·4$, and pure blue at $p_H = 1·5$. It seems that the pink colour is due to a minimal adsorption, which can be induced both by extreme lowering of the iodine content of the solution, and by lowering in concentration of the hydrogen ion.

With respect to other ions, Mylius (*Ber.*, 1887, **20**, 688) first pointed out that starch iodide is not formed in the absence of iodide ions. A preponderant effect of these ions can also be shown with benzoyl-β-methylumbelliferone. Experimentally it is difficult to exclude iodide ions completely, and we contented ourselves by reducing them to a minimum by using dilute ($N/1000$) alcoholic iodide solution, freshly prepared in the cold. This was mixed with the alcoholic solution of the organic substance and then with 0·2 molar solution of the following potassium salts: Iodide, chloride,

bromide, nitrate, sulphate, acetate, tartrate, citrate, thiocyanate. The blue colour appeared most rapidly when the iodide, and not at all when the thiocyanate, was used. The other salts were intermediate, but did not show sufficiently marked differences among themselves to allow of their being arranged in a series.

There is no indication of a lyotropic effect; the inhibition by the thiocyanate is secondary, due to its removing free iodine from the solution. The iodide ion has here a specific effect, although it is to some extent replaceable by other ions. We obtained a similar result with benzylidenephthalide.

Dr. R. C. Menzies has called our attention to a reaction of thallous salts which at least simulates the formation of the iodine addition compounds described in this paper. We find that it may be used to illustrate the necessary presence of iodide ions in a striking manner. If to 2 c.c. of a cold saturated aqueous solution of thallous chloride, 2 drops (= 0·04 c.c.) of a $N/5$-alcoholic iodine solution are added, the resultant solution is clear and has a pale brown colour. Addition of a few drops of a potassium iodide solution at once produces an intense greyish-black precipitate, which disappears on warming and returns on cooling, as in the case of starch iodide. The precipitate doubtless consists of the higher iodide $TlI_8$, the conditions of whose stability have been closely investigated by Abegg and Maitland (*Z. anorg. Chem.*, 1906, **49**, 341), but it is not formed at all readily from pre-formed thallous iodide, but only when this iodide is precipitated in the presence of free iodine. The need of iodide ions in the formation of starch iodide and similar substances might simply result from the fact that these blue compounds are periodides. That blue iodine additive compounds are so largely given by pyrone derivatives, would depend on the basic nature of the latter, enabling an iodide to be formed, which then adds more iodine. In the starch molecule we may attribute basic properties to the bridge oxygen atom. Incidentally, the fact that thallous iodide, basic lanthanum acetate, and a variety of organic compounds all give a similar reaction makes the search for a constitutive factor rather illusory. It is more important to consider the molecular weight. Thallous chloride and coumarin give greyish-black, crystalline additive compounds, whereas basic lanthanum acetate, being highly colloidal, gives a pure blue addition compound, characteristic of starch and other organic substances of high molecular weight.

*Distribution of Iodine between Solution and Adsorbent.*—Küster (*Annalen*, 1894, **283**, 366) first showed that the composition of starch "iodide" changes continuously with the iodine content of the solution, in a manner which is now held to be characteristic of

adsorption. A similar relationship was observed by Biltz (*Ber.*, 1904, **37**, 719) for basic lanthanum acetate and by Barger and Field (J., 1912, **101**, 1402) for the glucoside saponarin. In all these cases, the "iodide" is amorphous. On the other hand, the blue crystals formed from cholalic acid have, over a certain range of iodine concentration of the solution, a constant iodine content corresponding more or less to Mylius' formula, $(C_{24}H_{40}O_5I)_4,KI$. As this case stood by itself, we have examined a few cases of simple substances (coumarin, acetocoumarin) which form mixed crystals with iodine, together with benzoyl-β-methylumbelliferone, which forms an amorphous adsorption compound. The method used was the same as that employed for cholalic acid by Barger and Field. The organic solvent of the first two substances was alcohol, of the last-named, glacial acetic acid; $C$ = milligram-atoms of iodine per litre left in solution; $x/m$ = gram-atoms of iodine per molecule of organic substance separated out.

*Coumarin.*

I. $m = 0{\cdot}3$ millimole.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $C$ ..... | 7·0 | 8·7 | 10·4 | 13·9 | 17·4 | 32·9 | 65·8 | 114 | 164 |
| $x/m$ ... | 0·208 | 0·258 | 0·292 | 0·357 | 0·417 | 0·55 | 0·57 | 0·57 | 0·57 |

II. $m = 0{\cdot}4$ millimole.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $C$ ..... | 10·3 | 13·2 | 17 | 33 | 49 | 82·3 | 148 | 164 |
| $x/m$ ... | 0·27 | 0·34 | 0·40 | 0·55 | 0·63 | 0·63 | 0·67 | 0·67 |

*Acetocoumarin.*

$m = 0{\cdot}1$ millimole.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $C$ ..... | 6·7 | 8·6 | 17·0 | 33·9 | 42·4 | 50·9 | 55·3 | 73·7 | 133 | 168 |
| $x/m$ ... | 0·326 | 0·337 | 0·369 | 0·369 | 0·421 | 0·463 | 0·515 | 0·642 | 0·69 | 0·71 |

*Benzoyl-β-methylumbelliferone.*

$m = 0{\cdot}2$ millimole.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $C$ ..... | 8·6 | 17·2 | 24·7 | 32·9 | 41·2 | 100 | 167 |
| $x/m$ ... | 0·091 | 0·163 | 0·55 | 0·73 | 0·775 | 0·845 | 0·86 |

We attach most importance to the results with coumarin, which, under the conditions employed, always separated as homogeneous, steel-grey crystals. These evidently have a variable composition, unless the iodine content of the solution is sufficiently high. Even then, $x/m$ does not reach unity. We at first considered that the figures quoted would be subject to a correction for coumarin remaining in the solution, but continuous extraction of the latter by ether only revealed a trace of this compound.

This research was rendered possible by a grant to one of us (F. J. E.) from the Department of Scientific and Industrial Research.

The cost of materials used was met by a grant of the Moray Research Fund of this University. For both grants we wish to express our gratitude.

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UNIVERSITY OF EDINBURGH. [*Received, September 9th*, 1924.]

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# CCCXXX.—*Studies of Electrolytic Polarisation. Part I. The Cathodic Overvoltage of Lead.*

By SAMUEL GLASSTONE.

IN a previous paper (this vol., p. 250), a commutator method for the determination of overvoltage has been developed and applied to the study of the lead electrode in *N*-sulphuric acid and sodium hydroxide at current densities ranging from 0·0008 to 0·24 amp. per sq. cm. The object of the present work was to extend these measurements to electrolytes of varying hydrogen-ion concentration, and also to measure the minimum overvoltage, that is, the overvoltage at which visible gas evolution in the form of bubbles is first observed (compare Caspari, *Z. physikal. Chem.*, 1899, **30**, 89), in different electrolytes. An examination of the literature has revealed no previous study of the minimum overvoltage of any electrode in solutions of varying hydrogen-ion concentration, except a few isolated observations made by Thiel and Breuning (*Z. anorg. Chem.*, 1913, **83**, 329) on the iron electrode. In the present paper, a detailed study of the lead electrode is described and discussed.

When a polarised electrode is in a state of equilibrium, the amount of hydrogen liberated by the current is balanced by the amounts removed by the two chief compensating processes, namely bubble formation and diffusion, assuming that the electrolyte does not contain a depolariser. The quantity of gas set free at the electrode in a given time is proportional to the current density, $I$, and hence may be written as equal to $k_1 I$, where $k_1$ is a constant. The rate at which gas is removed in the form of bubbles is probably a function of the total concentration of gas at the electrode, namely $C$, and may be put equal to $k_2 C^m$, where $k_2$ and $m$ are constants for a given electrode and electrolyte. Further, if we assume that the layer of electrolyte near the electrode has a definite solubility limit for hydrogen gas, then when this limiting condition is reached the rate at which gas can be removed from the electrode by diffusion must be a constant, independent of the actual concentration of gas at the electrode. Let us suppose that this condition exists and that the rate of removal of hydrogen from the electrode by the

process of diffusion is equal to a constant $k_3$; therefore we have, at equilibrium,

$$k_1 I = k_2 C^m + k_3.$$

As the current density is increased, so there is an increase in the amount of electromotively active material and a corresponding increase in the molecular hydrogen accumulated at the electrode; we may therefore assume that the total concentration of gas, $C$, is a function of $H$, the concentration of active material, and write $C = k_4 H^n$, where $k_4$ and $n$ are constants for a given electrode and electrolyte. Combining this expression with the one given above, we arrive at the following equation:

$$H = (yI - z)^x,$$

where $x$, $y$, and $z$ are constants. If we may regard overvoltage as due to the potential of an electrode which is reversible with respect to the particular electromotively active material which has accumulated at it, then for a given electrolyte at constant temperature we may write

$$E = A + B \log H,$$

where $E$ is the overvoltage, and $A$ and $B$ are constants. Substituting in this the value for $H$ that has been obtained above, and simplifying the constants, we arrive at the expression

$$E = a + b \log (I - c),$$

where $a$, $b$ and $c$ are constants for the given electrode and electrolyte at constant temperature.

This equation differs from the conventional equation in so far as it involves a third constant $c$, and it is certainly in excellent agreement with the facts as long as bubble formation is taking place; this may be seen from Table I. At high current densities, $c$, which is fairly small, may be neglected in comparison with $I$, and so the behaviour of the electrode may be represented by the simpler equation, $E = a + b \log I$.

TABLE I.

| Lead cathode in $N$-$H_2SO_4$. $E = 0{\cdot}59 + 0{\cdot}115 \log (I - 16{\cdot}5)$. | | | Lead cathode in $N$-NaOH. $E = 0{\cdot}44 + 0{\cdot}2 \log (I - 12{\cdot}0)$. | | |
|---|---|---|---|---|---|
| $I$ (milliamps.). | $E$ (obs.). | $E$ (calc.). | $I$ (milliamps.). | $E$ (obs.). | $E$ (calc.). |
| 18 | 0·60 | 0·61 | 14 | 0·52 | 0·50 |
| 20 | 0·645 | 0·65 | 16 | 0·56 | 0·56 |
| 30 | 0·725 | 0·72 | 20 | 0·61 | 0·62 |
| 40 | 0·76 | 0·75 | 36 | 0·70 | 0·715 |
| 50 | 0·78 | 0·765 | 60 | 0·78 | 0·775 |
| 90 | 0·82 | 0·805 | 120 | 0·85 | 0·8 |
| 150 | 0·84 | 0·835 | 240 | 0·90 | 0·91 |
| 300 | 0·86 | 0·87 | | | |
| 600 | 0·88 | 0·905 | | | |

The agreement between the observed and calculated values is quite good; at high current densities it is obvious that the constant $c$ may be neglected, but its influence is considerable with smaller currents. If the amount of gas that diffuses from the electrode is small, the constant $c$ will be small, and consequently the behaviour of the electrode will be well represented by the simpler logarithmic equation even at low current densities; in these circumstances, the "residual current" that can flow without producing visible evolution of gas is of course very small. This is the case with the mercury cathode in sulphuric acid.

In developing the simpler logarithmic formula, Tafel (*Z. physikal. Chem.*, 1905, **50**, 668) and Westrip (this vol., p. 1112) have assumed that the current is proportional to the rate at which atomic hydrogen is removed in the form of molecules; thus no allowance is made for the atomic hydrogen that may be removed either by diffusion into the electrode or electrolyte, or together with molecular hydrogen in the form of gas bubbles. This omission will probably not be very serious at high current densities, but for small currents an appreciable correction is necessary and the simple logarithmic formula will not hold good. By correcting for the amount of atomic hydrogen removed in other ways than as the molecular form, equations may be developed which are similar to the one deduced above.

If a large cathode is polarised with a small current, then almost all the hydrogen liberated by the current will diffuse away as fast as it is formed, and so the potential of the electrode will become only slightly more negative. As the current density is increased, however, either atomic or molecular hydrogen, or more likely both, will accumulate rapidly at the electrode, until there is a sufficient concentration of gas to cause bubble formation to commence; during this period the cathodic potential will increase rapidly as the current is increased. The advent of bubble formation introduces a new and efficient compensating process for the removal of the hydrogen that accumulates at the electrode, and so now, on increasing the current, the rise in potential will be less than before. Consequently, in the case of a gas like hydrogen which is not very soluble in the electrolyte, and with a cathode that does not adsorb the gas too readily, the current–potential curve should show a break at the potential at which bubble formation commences. Westhaver (*Z. physikal. Chem.*, 1905, **51**, 65), however, has pointed out that since the current–potential curves are logarithmic in nature, the position of the apparent point of inflection in the curve will depend on the relation between the scales employed for the representation of the current and potential. This author recommends that the

potential of the electrode should be plotted against the *logarithm* of the current, and claims that the curve so obtained shows a distinct and definite break at the potential corresponding with the formation of bubbles. An examination of the formula $E = a + b \log (I - c)$ will show, however, that the slope of Westhaver's curve, $dE/d(\log I)$ is equal to $bI/I - c$, and hence will decrease steadily as the current density, $I$, increases, but may be quite large soon after bubble formation has commenced, when $I$ and $c$ are almost equal; consequently, in some cases the break in the curve at the point of bubble formation will not be very marked. The graphical method of determining the minimum overvoltage may therefore not be very trustworthy in some cases, and it is considered advisable that it should be used only to confirm the results obtained by the observation method of Caspari (*loc. cit.*) and Thiel and Breuning (*loc. cit.*).

## Experimental.

Previous workers on the subject of minimum overvoltage have employed electrodes consisting of short wires of indefinite area; in the present work it was desired to extend the measurements to include overvoltages at higher current densities for the same electrode, and consequently a slight sacrifice of accuracy was made by using an electrode of 7·5 sq. cm. exposed area. The same conventional arrangement of apparatus was used as had been employed in previous work (*loc. cit.*); the circuit contained no special inductance and was so arranged that it could be completely broken by means of a commutator. The standard half-element in use was the saturated calomel electrode, and no correction was made for diffusion potential. Connexion between the test and standard electrodes was made in the usual manner by means of a tube ending in a fine jet, which was placed in close contact with the former electrode. As a rule, the anode and cathode compartments were not separated, but in a few experiments in which this separation was made the results were found to be unchanged.

In determining the point at which bubble formation commences, Thiel and Breuning (*loc. cit.*) have shown that there is a danger of the electrode becoming supersaturated with gas owing to the retardation of the bubble-forming process. These authors recommend that a fairly large current should be applied so that bubble formation occurs freely, and that the current should then be reduced until the point is reached at which bubbles leave the electrode at the rate of not more than one in 2 minutes; from the potential at this point the minimum overvoltage may be determined. With a lead electrode, that had been roughened by previous use, as a cathode, the danger of supersaturation was found to be very small,

but in the course of the present work the method of Thiel and Breuning was generally used.

The clean lead electrode was first used as a cathode in sulphuric acid until its surface was no longer bright. It was then set up as an electrode in the particular electrolyte which was being studied, and the polarising current put on until bubbles of gas were evolved freely. The current was then decreased gradually, and after allowing 10 minutes for the electrode to reach a steady state, it was observed for 2 minutes to see if any bubbles were being liberated Measurements were also made by the graphical method described above, and the results quoted below are usually the mean of a number of different observations made by both methods.

It has been suggested (Newbery, *J. Amer. Chem. Soc.*, 1920, **42**, 2007) that at very low current densities the potential of an electrode measured by the direct method is due almost entirely to a resistance, whereas observations by the present author have indicated that at current densities of the order of 1 milliamp. per sq. cm. the potential measured by the direct method is a real electrode potential which is almost identical with the instantaneous back *E.M.F.* at the moment that the current is switched off. At still lower current densities, however, difficulties were experienced in the previous work on the measurement of back *E.M.F.* (*loc. cit.*), owing to the fact that when the commutator was working, the polarised electrode failed to reach its normal equilibrium on account of the removal of electromotively active material from it during the periods in which the current was off. This difficulty has been overcome to a great extent by arranging the commutator (J., 1923, **123**, 2926) so that the polarising current was only off for about one-sixth of a complete cycle; under these conditions, the potential reached while the current was flowing was the same whether the commutator was working or not, even at very low current densities. By measuring the back *E.M.F.* at 0·002, 0·004, 0·006 and 0·008 sec. after the polarising current was switched off, and extrapolating the *P.D.*–time curve to zero time, as described in previous work, the instantaneous back *E.M.F.* of the electrode has been found to be almost identical with the potential measured by the direct method. This holds at very small current densities as long as gas bubbles are being evolved from the electrode; if the current is too small for this to occur, then the rate of fall of the back *E.M.F.* is so great that reasonably accurate extrapolation is not possible. In subsequent work, therefore, the direct method has been used for measuring the potentials of polarised electrodes at all currents up to 0·005 amp., and frequently up to 0·01 amp., when the electrolyte was not too dilute; at higher current values, the commutator

extrapolation method, developed by the present writer, has been used.

All the experiments were carried out at room temperature, which was approximately 15°.

*Results.*

For the sake of convenience, the results have been divided into three sections; the first deals with sulphuric acid electrolytes, the second with sodium hydroxide and other alkaline solutions, and the last with solutions of varying hydrogen-ion concentration in which only the minimum overvoltage has been determined. Unless otherwise stated, the results are given as overvoltages.

*Sulphuric Acid Solutions.*

TABLE II.

| | Current density (amp./cm.²). | | | | | |
|---|---|---|---|---|---|---|
| Electrolyte. | Minimum. | 0·0007. | 0·002. | 0·004. | 0·008. | 0·016. |
| 8*N*-$H_2SO_4$ | 0·62 | 0·64 | 0·74 | 0·77 | 0·80 | 0·82 |
| *N*-$H_2SO_4$ | 0·62 | 0·64 | 0·76 | 0·79 | 0·81 | 0·84 |
| *N*/16-$H_2SO_4$ | 0·62 | 0·64 | 0·77 | 0·81 | 0·83 | 0·86 |

TABLE III.

| C.D. | *N*/16-$H_2SO_4$. *N*/16-$K_2SO_4$. | *N*/16-$H_2SO_4$. *N*/4-$K_2SO_4$. | *N*/16-$H_2SO_4$. *N*-$K_2SO_4$. |
|---|---|---|---|
| (Minimum) | (0·62) | (0·62) | (0·62) |
| 0·002 | 0·82 | 0·85 | 0·89 |
| 0·004 | 0·88 | 0·90 | 0·97 |
| 0·008 | 0·95 | 0·95 | 1·09 |
| 0·016 | 1·05 | 1·21 | 1·19 |
| 0·032 | 1·27 | 1·27 | 1·24 |
| 0·06 | 1·33 | 1·31 | 1·30 |
| 0·12 | 1·37 | 1·36 | 1·36 |

The results given in Table II show that a change in the concentration of the sulphuric acid from 8*N* to *N*/16, that is, an approximately thirty-fold decrease in the hydrogen-ion concentration, causes very little alteration either in the minimum overvoltage or in that at a definite current density. When potassium sulphate is added to the electrolyte, there is very little alteration in the hydrogen-ion concentration, and there is also no change in the minimum overvoltage (Table III); at higher current densities, however, considerable variations from the overvoltage in sulphuric acid alone are observed. Similar divergences were noted when sodium sulphate was added to dilute sulphuric acid. In these circumstances, the discharge of sodium- or potassium-ions to form alkali metal-lead alloys with the material of the cathode (compare Haber and Sack, *Z. Elektrochem.*, 1902, **8**, 245; Haber, *ibid.*, p. 541; Sack, *Z. anorg. Chem.*, 1903, **34**, 286) appears to be possible in addition

to the normal discharge of hydrogen-ions. The results indicate that above a certain current density the cathodic potential increases very rapidly, probably because an alkali metal–lead alloy is accumulating at the electrode, and then more slowly as the electrode becomes saturated with this alloy at a cathodic potential of about 1·3 volts; at still higher current densities, there appears to be another increase of potential due to the formation of a second alloy (compare Haber, *loc. cit.*). The potentials measured in the solutions containing alkali-metal ions cannot therefore be regarded as depending solely on the lead electrode and the hydrogen-ion concentration; they depend also on the alkali-metal concentration in the electrolyte.

*Alkaline Solutions.*

The following table gives the cathodic *potentials* of a lead electrode in *N*-sodium hydroxide and in *N*-sodium phosphate solution.

TABLE IV.

| | Current density (amp./cm.²). | | | | |
|---|---|---|---|---|---|
| Electrolyte. | 0·0005. | 0·0013. | 0·004. | 0·008. | 0·016. |
| *N*-NaOH | 1·33 | 1·51 | 1·66 | 1·71 | 1·75 |
| *N*-$Na_2HPO_4$ | 1·33 | 1·50 | 1·68 | 1·73 | 1·78 |

Within the limits of current density quoted above, a lead electrode exhibits almost the same cathodic potential in *N*-sodium hydroxide and in *N*-sodium phosphate, although the hydrogen-ion concentration is almost one hundred thousand times as great in the latter solution as it is in the former. It appears, therefore, that in these circumstances, when the hydrogen-ion concentration is very small, the cathodic potential depends mainly on the alkali-metal ion concentration, and hence it does not seem justifiable to compare the overvoltages calculated from these potentials with those obtained in solutions containing hydrogen-ions as the only positive ions. In extending the overvoltage measurements to solutions containing small concentrations of hydrogen-ions, it is obviously necessary to resort to the use of various " buffer solutions " and other solutions containing alkali-metal ions; consequently, great caution must be exercised in choosing the conditions for the measurement of overvoltage, so that the results may be comparable with one another. Experiments have shown that at appreciable current densities the cathodic potentials in the buffer solutions are uncertain and dependent on the concentration of alkali-metal ion in the electrolyte. The minimum overvoltage, on the other hand, appeared to be quite definite and reproducible, and almost independent of the alkali-metal ion concentration as in the case of the sulphuric acid elec-

trolytes quoted above (Table III); the results obtained with various electrolytes are given below.

*The Minimum Overvoltage.*

The electrolytes used were Sörensen borate and citrate buffers varying in $p_H$ from 1·9 to 12·6; they were made up according to the directions given by Clark in "The Determination of Hydrogen Ions," 1922, p. 107 *et seq.*, except that sulphuric acid was used instead of hydrochloric acid in order to avoid the evolution of chlorine at the anode. The hydrogen-ion concentrations were always checked by means of the hydrogen electrode. The accompanying table contains a complete list of the minimum overvoltages that have been determined with the lead cathode.

TABLE V.

| Electrolyte. | $p_H$. | Min. ov. | Electrolyte. | $p_H$. | Min. ov. |
|---|---|---|---|---|---|
| $H_2SO_4$ | 1·0 | 0·62 | Borate + $H_2SO_4$ | 8·0 | 0·65 |
| Citrate + $H_2SO_4$ | 1·9 | 0·62 | ,, ,, | 9·0 | 0·63 |
| ,, ,, | 3·0 | 0·63 | $N$-$Na_2HPO_4$ | 9·0 | 0·62 |
| ,, ,, | 4·0 | 0·64 | Borate + NaOH | 10·1 | 0·65 |
| ,, + NaOH | 5·0 | 0·63 | ,, ,, | 11·2 | 0·60 |
| ,, ,, | 6·0 | 0·66 | ,, ,, | 12·6 | 0·52 |
| $N$-$Na_2SO_4$ | 7·0 | 0·63 | $N$/16-NaOH | 13 | 0·52 |
| $N$-$K_2SO_4$ | 7·0 | 0·64 | $N$-NaOH or -KOH | 14 | 0·48 |

The present author has suggested that the minimum overvoltage may be regarded as due to the concentration of atomic hydrogen at the electrode when the total gas accumulation is just sufficient to overcome the forces at the electrode–electrolyte–gas interfaces, so that bubble formation can commence (see *Trans. Faraday Soc.*, 1924, **19**, 808). If we assume that the surface tension forces do not vary very greatly as the nature of the electrolyte is altered—this is probably the case with most of the solutions dealt with—then it follows that the concentration of gas necessary before bubble formation can commence will be roughly constant. Further, if the ions present exert no catalytic influence on the reaction $2H \longrightarrow H_2$, then it is clear that the minimum overvoltage for a given electrode will be independent of the hydrogen-ion concentration of the electrolyte. The results quoted above show that this concentration may be changed from 1 to $1 \times 10^{-11}$ gm.-ion per litre, yet the minimum overvoltage is only altered by a comparatively small amount, which may be due to experimental error or to variations in the electrode surface. Judging from the results obtained with various concentrations of sulphuric acid (Table II), the overvoltage at appreciable current densities would probably also be independent of the nature of the electrolyte if the alkali-metal ions exerted no disturbing influence.

When the hydrogen-ion concentration in the electrolyte is very small, there is a distinct diminution in the minimum overvoltage from the normal value of 0·62 volt down to 0·48 volt. In the case of *N*-sodium or potassium hydroxide the minimum overvoltage corresponds to a cathodic potential of 1·?9 volts; this is the same potential at which the surface of the lead electrode appears to approach saturation with the first alkali metal-lead alloy (see p. 2420). It is possible, therefore, that the diminution in overvoltage may be due to the change in the nature of the electrode surface, especially as it has been observed that an alloy often has a lower overvoltage than either of the constituent metals (see, for example, Glasstone, *ibid.*, p. 574). The decrease in minimum overvoltage may also be due to a decrease in the interfacial forces, or to the possibility that hydroxyl ions in large concentration can catalyse the reaction $2H \longrightarrow H_2$, so that for the same total gas concentration as in other cases there is a smaller proportion of atomic hydrogen; it is possible that one, two, or all three factors mentioned above may be operative at the lead electrode. This diminution in overvoltage in alkaline electrolytes has been noted with other metals; the results of Thiel and Breuning (*loc. cit.*) indicate that the minimum overvoltage at the iron electrode in alkaline solution is about 0.08, whilst the normal value in acid electrolyte is considered to be 0·175 volt. Preliminary experiments by the present author have shown that copper has a minimum overvoltage of about 0·20 in sulphuric acid, but only 0·12 volt in *N*-sodium hydroxide. With a mercury cathode, however, this decrease of overvoltage in alkaline solution has not been observed. It is therefore not yet possible to draw any definite conclusions regarding this phenomenon.

*Electrode Surface.*—It has been found that the minimum overvoltage at a bright lead surface is about 0·67 volt in sulphuric acid and 0·55 in alkali, whereas after the surface has been roughened by use as a cathode the overvoltage is reduced to 0·62 and 0·48, respectively. The actual value of the minimum overvoltage is probably independent of the electrode surface area, since the same results may be obtained with a large or small electrode, and so the diminution of overvoltage that results from a roughening of the surface must be due either to an increased catalytic influence on the reaction $2H \longrightarrow H_2$, or to a diminution of the interfacial forces, or to both these factors. It should therefore be clearly realised that the lower overvoltages at appreciable current densities that result from a roughening of the electrode surface, for example, when smooth platinum is platinised, are due, not only to the reduced current density, but also to other factors such as those mentioned above.

*Summary.*

(1) It is shown that in the deduction of the formula $E = a + b \log I$, where $E$ is the overvoltage and $I$ the current density, previous authors have neglected to account for the electromotively active material removed from the electrode by diffusion; by allowing for this, the formula $E = a + b \log (I - c)$, where $a$, $b$, and $c$ are constants, has been developed. It is in excellent agreement with observations made on a lead cathode.

(2) The uncertainty of the graphical method for the determination of the minimum overvoltage is discussed.

(3) As long as bubble formation is taking place, the potential of an electrode at small current density measured by the direct method is almost identical with the instantaneous back *E.M.F.*

(4) At appreciable current densities, the cathodic potential of a lead electrode is influenced by the presence of alkali-metal ions in the electrolyte; the minimum overvoltage, however, does not appear to be greatly affected. The latter quantity is almost constant for all hydrogen-ion concentrations between 1 and $10^{-11}$ gm.-equiv. per litre; in more alkaline solution, there appears to be a decrease in the minimum overvoltage of lead. These observations are discussed from a theoretical standpoint.

(5) The minimum overvoltage has been found to decrease somewhat as the electrode surface is roughened. The importance of this observation in connexion with overvoltage at a definite current density is discussed.

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## CCCXXXI.—*Halogen-substituted 1-Arylpyrazolones.*

By FREDERICK DANIEL CHATTAWAY and CHARLES RICHARD NÖEL STROUTS.

THE 1-chlorophenyl-3-methyl-5-pyrazolones are very similar in properties to the unsubstituted base, neither the position of the substituted halogen nor its accumulation in the phenyl residue appearing greatly to affect the reactivity of the methylene group. They all react with methyl iodide to form chloro-substituted 1-phenyl-2 : 3-dimethyl-5-pyrazolones. These differ in one respect markedly from antipyrine, their aqueous solutions have an extremely bitter taste.

## Experimental.

1-o-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*, $\begin{matrix}MeC{=}N\\ H_2C{\cdot}CO\end{matrix}\!>\!N{\cdot}C_6H_4Cl$, is best prepared by heating the *o*-chlorophenylhydrazone of aceto-acetic ester at 150—170° for about 90 minutes, until the evolution of alcohol ceases. The pyrazolone, which remains behind as a viscous, dark red oil that solidifies on cooling, separates from hot alcohol, in which it is fairly easily soluble in small, glistening, white prisms, m. p. 199° (Found : Cl = 17·01. $C_{10}H_9ON_2Cl$ requires Cl = 17·00%).

The *hydrochloride*, which separates in small, glistening, white needles on cooling a solution of the pyrazolone in excess of hot concentrated hydrochloric acid, melts at 154° and on further heating decomposes at 172° into the pyrazolone and hydrogen chloride (Found : Cl = 28·45. $C_{10}H_9ON_2Cl,HCl$ requires Cl = 28·95%).

The 4-*oximino*-derivative separates immediately as a canary-yellow solid when a well-cooled solution of 1-*o*-chlorophenyl-3-methyl-5-pyrazolone (1 g.) and sodium nitrite (0·4 g.) in a little aqueous caustic soda is run into an excess of dilute hydrochloric acid, cooled in a freezing mixture. It is sparingly soluble in boiling water, and crystallises from dilute alcohol in long, golden-brown prisms, m. p. 174°. It dissolves in caustic soda, giving a fine red solution, and may be reprecipitated unchanged by dilute mineral acids (Found : Cl = 15·10. $C_{10}H_8O_2N_3Cl$ requires Cl = 14·93%).

The 4-*benzylidene* derivative is moderately easily soluble in boiling alcohol, from which it separates in glistening, orange-coloured, flattened, rhombic prisms, m. p. 159° (Found : Cl = 12·09. $C_{16}H_{13}ON_2Cl_3$ requires Cl = 11·96%).

1-o-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*-4-*azo*-o-*chlorobenzene*, $\begin{matrix}MeC{=}N\\ C_6H_4Cl{\cdot}N_2{\cdot}CH{\cdot}CO\end{matrix}\!>\!N{\cdot}C_6H_4Cl$, separates from a mixture of chloroform and alcohol in glistening, golden-yellow prisms, m. p. 212° (Found : Cl = 20·59. $C_{16}H_{12}ON_4Cl_2$ requires Cl = 20·44%).

1-o-*Chlorophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* (o-*Chloroantipyrine*), $\begin{matrix}MeC{\cdot}NMe\\ HC{-}CO\end{matrix}\!>\!N{\cdot}C_6H_4Cl$, prepared by heating a mixture of 4·1 g. of 1-*o*-chlorophenyl-3-methyl-5-pyrazolone, 2·9 g. of methyl iodide, and 15 c.c. of dry methyl alcohol in a sealed tube at 100—120° for 10 hours, is easily soluble in hot toluene, from which it separates in wax-like, colourless, rhombic crystals, m. p. 113°. The base is very soluble in water, giving a solution which has a strong bitter taste (Found : Cl = 15·81. $C_{11}H_{11}ON_2Cl$ requires Cl = 15·93%).

1-m-*Chlorophenyl*-3-*methyl*-5-*pyrazolone* is moderately easily soluble in alcohol, from which it separates in small, colourless prisms, m. p. 131° (Found : Cl = 17·06. $C_{10}H_9ON_2Cl$ requires Cl = 17·00%).

The *hydrochloride* separates, on cooling a solution of the pyrazolone in excess of hot concentrated hydrochloric acid, as a pulpy mass of white, felted needles, m. p. 184° (with decomp. into the pyrazolone and hydrogen chloride) (Found : Cl = 28·84. $C_{10}H_9ON_2Cl,HCl$ requires Cl = 28·95%).

The 4-*oximino*-derivative is sparingly soluble in boiling water, from which it separates in fine, hair-like, orange needles, m. p. 173° (decomp.) (Found : Cl = 14·98. $C_{10}H_8O_2N_3Cl$ requires Cl = 14·93%).

The 4-*benzylidene* derivative separates from hot alcohol, in which it is fairly easily soluble, in fine, felted, red needles, m. p. 128° (Found : Cl = 12·02. $C_{16}H_{13}ON_2Cl$ requires Cl = 11·96%).

1-m-*Chlorophenyl*-3-*methyl*-4-iso*propylidene*-5-*pyrazolone*,

$$\begin{matrix} MeC{=}N \\ CMe_2{\cdot}C{\cdot}CO \end{matrix}\!\!>\!N{\cdot}C_6H_4Cl,$$

obtained by heating 1 g. of the pyrazolone with 4 g. of boiling acetone for 4 hours, and pouring the resulting yellow solution into water, separates from hot alcohol, in which it is easily soluble, in felted, sulphur-yellow needles, m. p. 110° (Found : Cl = 14·34. $C_{13}H_{13}ON_2Cl$ requires Cl = 14·27%).

1-m-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*-4-*azo*-2′ : 4′-*dichlorobenzene* separates from a mixture of chloroform and alcohol in small, golden-brown needles, m. p. 190° (Found : Cl = 27·97. $C_{16}H_{11}ON_4Cl_3$ requires Cl = 27·89%).

1-m-*Chlorophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* (m-*Chloroantipyrine*) separates from a mixture of chloroform and ligroin in glistening plates, m. p. 89—90°. The base is somewhat soluble in water, to which it imparts an extremely bitter taste, and very soluble in alcohol, chloroform, or ether (Found : Cl = 13·67. $C_{11}H_{11}ON_2Cl$ requires Cl = 15·93%).

m-*Chloropyrazole-blue*, $C_6H_4Cl{\cdot}N\!<\!\begin{matrix} N{=}CMe & CMe{:}N \\ CO{\cdot}C{=}C & C{-}CO \end{matrix}\!>\!N{\cdot}C_6H_4Cl$.—Two grams of bis-1-*m*-chlorophenyl-3-methyl-5-pyrazolone (prepared by heating the pyrazolone, 2 g., with phenylhydrazine, 0·3 g., until ammonia is no longer liberated) and an excess of sodium nitrite are dissolved in caustic soda solution and added to an excess of dilute sulphuric acid, and the curdy precipitate of m-*chloropyrazole-blue* is well boiled to coagulate it, collected, and washed with alcohol and ether. It separates from a solution in chloroform, on addition of much light petroleum as a fine, dark blue, crystalline powder,

m. p. 209° (decomp.). It is practically insoluble in all organic solvents except chloroform, in which it is only sparingly soluble and to which it imparts a fine deep blue colour. When rubbed, it acquires a metallic lustre. Reducing agents easily convert it back to the bis-pyrazolone.

*m*-Chloropyrazole-blue is also obtained when 1-*m*-chlorophenyl-3-methyl-5-pyrazolone is boiled with ferric chloride. The other chlorophenylmethylpyrazolones described in this paper give no trace of the corresponding pyrazole-blues when boiled with ferric chloride; the reactivity of the meta-compound in this respect being probably due to the fact that it is somewhat soluble in water, whereas the others are not (Found : Cl = 16·79. $C_{20}H_{14}O_2N_4Cl_2$ requires Cl = 17·17%).

The *hydrochloride* of 1-*p*-chlorophenyl-3-methyl-5-pyrazolone (Michaelis, *Annalen*, 1911, **385**, 93) forms small, glistening prisms, m. p. 194—195° (decomp. into the *p*-chlorophenylmethylpyrazolone and hydrogen chloride) (Found : Cl = 28·88. $C_{10}H_9ON_2Cl,HCl$ requires Cl = 28·95%).

The 4-*oximino*-derivative is very sparingly soluble in boiling water, from which it separates in long, orange, hair-like needles, m. p. 180° (decomp.) (Found : Cl = 15·14. $C_{10}H_8O_2N_3Cl$ requires Cl = 14·93%).

The compound is very soluble in most of the usual organic solvents. It may be recrystallised from alcohol, from which it separates in two polymorphic modifications. Of these, the unstable form appears as brick-red, compact, triclinic prisms. The stable form occurs as fine, orange needles. When the two forms were sealed up together in a little of the solvent, the compact form changed very slowly (after about a fortnight) into the needle modification.

The 4-*benzylidene* derivative is easily soluble in boiling alcohol, from which it separates in long, scarlet prisms, m. p. 156° (Found : Cl = 12·16. $C_{16}H_{13}ON_2Cl$ requires Cl = 11·96%).

1-p-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*-4-*azo*-p-*chlorobenzene* separates from much benzene in small, orange-red needles, m. p. 232° (Found : Cl = 20·59. $C_{16}H_{12}ON_4Cl_2$ requires Cl = 20·44%).

1-p-*Chlorophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* (p-*chloroantipyrine*) is easily soluble in hot toluene, from which it separates in glistening, flat plates, m. p. 126°. The compound is soluble in water, to which it imparts a very bitter taste, and in most of the usual organic solvents (Found : Cl = 16·00. $C_{11}H_{11}ON_2Cl$ requires Cl = 15·93%).

*Bis*-1-p-*chlorophenyl*-3-*methyl*-5-*pyrazolone*,

$$C_6H_4Cl\cdot N\langle \begin{matrix} N{=}CMe & CMe{\cdot}N \\ | & | \\ CO\cdot CH & CH\cdot CO \end{matrix} \rangle N\cdot C_6H_4Cl,$$

is formed when *p*-chlorophenylmethylpyrazolone is heated with

phenylhydrazine until ammonia is no longer liberated. It is almost insoluble in all organic solvents and separates as a fine, white, crystalline powder when a solution in caustic soda is acidified with hydrochloric acid. The bis-pyrazolone does not melt, but decomposes when strongly heated (Found: Cl = 17·23. $C_{20}H_{16}O_2N_4Cl_2$ requires Cl = 17·09%).

*p-Chloropyrazole-blue*, $C_6H_4Cl\cdot N<\begin{matrix}N{=}CMe & CMe{:}N\\ CO\cdot C & C{-}CO\end{matrix}>N\cdot C_6H_4Cl$, separates slowly from a chloroform solution, on addition of ether, in minute, blue needles. It is soluble in chloroform and in concentrated sulphuric acid, giving fine indigo-blue solutions. When rubbed, it shows a metallic lustre. It does not melt and is not volatile, but decomposes when heated at about 300°. Reducing agents easily reconvert it to the bispyrazolone (Found: Cl = 17·38. $C_{20}H_{14}O_2N_4Cl_2$ requires Cl = 17·17%).

1-2 : 4-*Dichlorophenyl*-3-*methyl*-5-*pyrazolone*, $\begin{matrix}CMe{=}N\\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_3Cl_2$, is fairly soluble in hot alcohol, from which it separates in short, glistening, white prisms, m. p. 178° (Found: Cl = 29·32. $C_{10}H_8ON_2Cl_2$ requires Cl = 29·19%). It is also soluble in hot concentrated hydrochloric acid, and, on cooling the solution, the *hydrochloride* separates in small, white needles. This melts at 153°, and, on further heating, decomposes at 170° into the pyrazolone and hydrogen chloride (Found: Cl = 38·21. $C_{10}H_8ON_2Cl_2$,HCl requires Cl = 38·07%).

The 4-*oximino*-derivative separates from much boiling water in very minute, fine, canary-yellow needles, m. p. 166—168° (decomp.) (Found: Cl = 25·99. $C_{10}H_7O_2N_3Cl_2$ requires Cl = 26·07%).

The 4-*benzylidene* derivative separates from boiling alcohol, in which it is easily soluble, in glistening, orange, rhombic crystals, m. p. 131° (Found: Cl = 21·48. $C_{17}H_{12}ON_2Cl_2$ requires Cl = 21·42%).

1-2 : 4-*Dichlorophenyl*-3-*methyl*-5-*pyrazolone*-4-*azobenzene* crystallises from alcohol in orange needles, m. p. 137—138° (Found: Cl = 20·52. $C_{16}H_{12}ON_4Cl_2$ requires Cl = 20·44%).

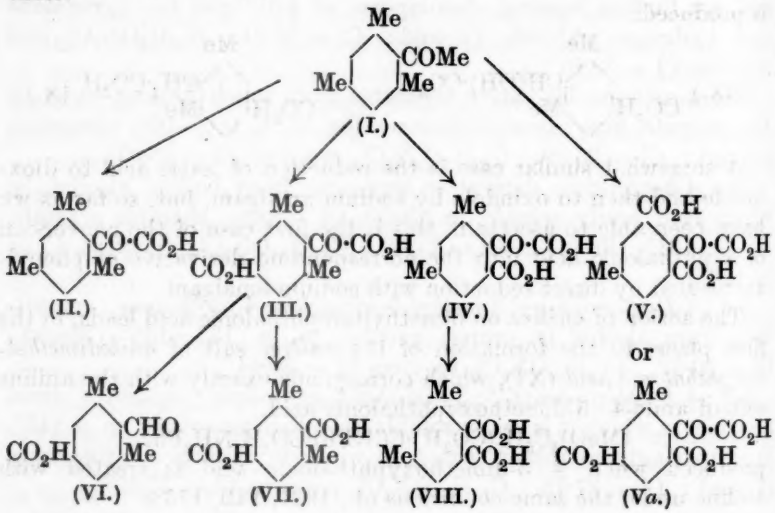
1-2 : 4-*Dichlorophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* separates from acetone, in which it is easily soluble, in colourless prisms, m. p. 143°. It is sparingly soluble in water, to which it imparts a bitter taste (Found: Cl = 27·78. $C_{11}H_{10}ON_2Cl_2$ requires Cl = 27·59%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, September 8th*, 1924.]

# CCCXXXII.—*The Oxidation of Acetomesitylene with Permanganate.*

By WILLIAM HENRY PERKIN, jun., and RICHARD ARTHUR BEATER TAPLEY.

THE oxidation of acetomesitylene (I) has been investigated by Feith (*Ber.*, 1891, **24**, 3543), V. Meyer and Molz (*Ber.*, 1897, **30**, 1272), van Scherpenzeel (*Rec. trav. chim.*, 1899, **19**, 379), Noyes (*J. Amer. Chem. Soc.*, 1898, **20**, 808; 1922, **43**, 925) and others and the conversion of this substance into mesitylglyoxylic acid (II) and into dimethylphthalic acid (VIII) and dimethylterephthalic acid (VII) has been described. The present communication deals with a more systematic examination of this oxidation and is a continuation of the investigations of Fargher and Perkin (J., 1921, **119**, 1724) and Kuroda and Perkin (J., 1923, **123**, 2094) of the properties of the phthalonic acids and their derivatives. The present inquiry has led to the isolation of a number of substances formed during the oxidation of acetomesitylene with permanganate which had not previously been described and the course of this oxidation, so far as it has now been established, is briefly summarised in the following table.




*Mesitylglyoxylic acid* (II) is produced in about 10 per cent. of the theoretical yield under the conditions we have employed; on oxidation with permanganate it is mainly converted into dimethylterephthalonic acid (III) and when reduced with sodium amalgam,

either in the cold or on the steam-bath, it yields 2 : 4 : 6-*trimethylmandelic acid*, $C_6H_2Me_3 \cdot CH(OH) \cdot CO_2H$.

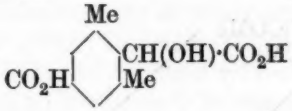
*Dimethylterephthalonic acid* (III), obtained in a yield of 13 per cent., forms a bisulphite derivative and a phenylhydrazone and the constitution of the acid is proved by its conversion into 2 : 6-dimethylterephthalic acid (VII) on heating with concentrated sulphuric acid or oxidation with permanganate. It is readily and completely esterified to the dimethyl ester,

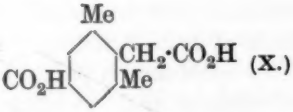
$$CO_2Me \cdot C_6H_2Me_2 \cdot CO \cdot CO_2Me,$$

by boiling with methyl alcohol and sulphuric acid. This behaviour is interesting when considered in connexion with the fact that 2 : 6-dimethylterephthalic acid yields, on esterification, the acid-ester to the extent of 97 per cent. (Hufferd and Noyes, *J. Amer. Chem. Soc.*, 1921, **43**, 925) and indicates that steric influence due to the two *o*-methyl groups does not extend beyond the carboxyl group attached to the benzene nucleus.

The *reduction* of dimethylterephthalonic acid has given unexpected results. When the sodium salt of the acid is left in contact with sodium amalgam in the cold, the reduction proceeds normally with the formation of 4-*carboxy*-2 : 6-*dimethylmandelic* acid (IX), but if the process is carried out at the boiling temperature, reduction proceeds further and 4-*carboxy*-2 : 6-*dimethylphenylacetic acid* (X) is produced.

(IX.)




(X.)

A somewhat similar case is the reduction of isatic acid to dioxindole and then to oxindole by sodium amalgam, but, so far as we have been able to ascertain, this is the first case of the conversion of a phthalonic acid into the corresponding derivative of phenylacetic acid by direct reduction with sodium amalgam.

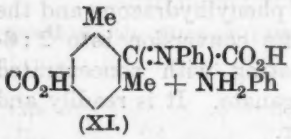
The action of *aniline* on dimethylterephthalonic acid leads, in the first place, to the formation of the *aniline* salt of *anilodimethylterephthalonic acid* (XI), which corresponds exactly with the aniline salt of anilo-4 : 5-dimethoxyphthalonic acid,

$$(MeO)_2C_6H_2(CO_2H) \cdot C(:NPh) \cdot CO_2H, NH_2Ph,$$

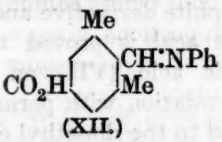
produced when 4 : 5-dimethoxyphthalonic acid is treated with aniline under the same conditions (J., 1921, **119**, 1738).

On hydrolysis with alkali, the aniline salt (XI) yields the free acid, which exhibits little tendency to crystallise but is at once converted into the same highly crystalline aniline salt when its solution in methyl alcohol is mixed with aniline (compare *loc. cit.*). When the aniline salt is boiled with water, or with xylene, it loses carbon

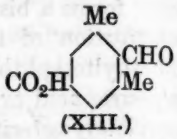
dioxide with the formation of *anilo-4-carboxy-2 : 6-dimethylbenzaldehyde* (XII), and, on hydrolysis with hydrochloric acid, this yields *4-carboxy-2 : 6-dimethylbenzaldehyde* (XIII).



(XI.)



(XII.)



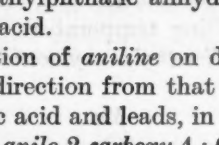
(XIII.)

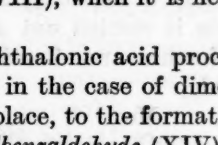
This new aldehydo-acid readily yields a phenylhydrazone, but the detailed examination of its properties must be reserved for a future communication.

4 : 6-*Dimethylphthalonic acid* (IV) is produced in very small quantities during the oxidation of acetomesitylene under the conditions we employed. It exhibits the remarkable property of crystallising from quite dilute hydrochloric acid in the *anhydrous* condition (m. p. 178°) but from water alone in the form of the *hydrate*, $CO_2H·C_6H_2Me_2·C(OH)_2·CO_2H$ (m. p. 86°); on heating on the steam-bath, the hydrate loses water with formation of the anhydrous acid. The constitution of the acid is proved by the fact that it yields 4 : 6-dimethylphthalic anhydride (cf. VIII), when it is heated with sulphuric acid.

The action of *aniline* on dimethylphthalonic acid proceeds in a different direction from that observed in the case of dimethylterephthalonic acid and leads, in the first place, to the formation of the *anilide* of *anilo-2-carboxy-4 : 6-dimethylbenzaldehyde* (XIV).

This substance is partly hydrolysed by boiling with concentrated hydrochloric acid, yielding the *anilide* of *2-carboxy-4 : 6-dimethylbenzaldehyde* (XV); the removal of the anilido-residue seems to be a difficult matter and has not yet been accomplished.

(XIV.)


(XV.)

*Methylcarboxyphthalonic acid* (V or Va) is probably produced in considerable amount during the oxidation of acetomesitylene, but its isolation, owing to its being deliquescent and very soluble in the usual media, is a matter of such difficulty that only a very small quantity has been obtained in a pure state. On reduction with sodium amalgam, it is converted into *methyldicarboxymandelic acid*, $C_6H_2Me(CO_2H)_2·CH(OH)·CO_2H$, which crystallises well and is not deliquescent.

## EXPERIMENTAL.

Acetomesitylene was prepared essentially as described by Böeseken (*Bull. Soc. chim.*, 1898, **19**, 349) and van Scherpenzeel (*Rec. trav. chim.*,

1899, **19**, 375), but with the modification of allowing the mixture of acetyl chloride, carbon disulphide, and aluminium chloride to stand for at least ½ hour before running in the mesitylene.

The following proportions give a yield of more than 90%; mesitylene (150 g.), aluminium chloride (200 g.), acetyl chloride (176 g.), carbon disulphide (600 c.c.).

*Oxidation of Acetomesitylene with Alkaline Permanganate.*—The ketone (25 g.) and potassium carbonate (13 g.) in water (260 c.c.) were stirred vigorously in a 2-litre flask fitted with a long condenser, and a boiling solution of permanganate (95 g.) in water (1 litre) was run in rapidly.

Oxidation started at once; after about 3 minutes the liquid boiled, and when this had subsided the whole was filtered, the colourless filtrate concentrated considerably on the steam-bath, made just acid with hydrochloric acid, then strongly alkaline with ammonia, excess of hot concentrated calcium chloride added, and the calcium oxalate and other salts filtered off while hot. The solid residue was then stirred with dilute hydrochloric acid until just acid to Congo, filtered, and the filtrate from calcium oxalate returned to the main bulk of the alkaline liquid. This was then gradually concentrated and the several crops of calcium salts submitted to a long process of fractional crystallisation, about nine fractions being ultimately collected. The first fraction consisted of colourless scales of calcium mesitylglyoxylate (II), the second was a mixture of this with calcium dimethylterephthalonate (III), the third was composed mainly of smaller crystals of the same salt, and the subsequent fractions were mixtures of this salt with calcium dimethylphthalonate (IV) and ammonium chloride. The mother-liquor still contained a considerable quantity of dimethylphthalonic acid, all the methylcarboxyphthalonic acid (V or Va), and other polybasic acids, and most of this mixture was recovered by repeated extraction with ether. After evaporation of the dried extract, a very viscid syrup remained (usually about 100 g. from 325 g. of acetomesitylene). On long standing, this deposited colourless needles of methylcarboxyphthalonic acid, which were collected, washed with sodium-dried benzene as rapidly as possible, and transferred to a vacuum desiccator (p. 2430). Since the oily filtrate did not deposit any more crystals on standing, it was esterified by boiling with methyl-alcoholic hydrochloric acid for several hours, and the mixed methyl esters isolated by adding water and extracting with ether. The ethereal solution was washed with sodium carbonate (A), dried, and fractionated under 15 mm., but considerable difficulty was experienced owing to the viscosity of the fractions. However, the fraction 190—205° partly solidified and, after contact with porous porcelain,

the colourless residue separated from methyl alcohol in prisms, melted at 85°, and proved to be the dimethyl dimethylterephthalonate (p. 2429), as a mixed melting point showed. The analysis of the fraction 210—214°/15 mm. indicated that it consisted essentially of the trimethyl ester of methylcarboxyphthalonic acid (Found: C = 58·2; H = 5·0. $C_{14}H_{14}O_7$ requires C = 57·1; H = 4·8%).

The sodium carbonate extract (A) yielded, on acidifying, a syrup which was dissolved in benzene and dried; the crystals which gradually formed separated from methyl alcohol in colourless needles, m. p. 155—156° (Found: C = 55·9; H = 4·5. $C_{13}H_{12}O_7$ requires C = 55·7; H = 4·2%). Since this substance is readily soluble in cold dilute sodium carbonate, it is probably the dimethyl-ester of methylcarboxyphthalonic acid.

*Mesitylglyoxylic Acid* (II).—The first fraction of the calcium salt was mixed with moderately concentrated hydrochloric acid and brought to the boil, when a heavy, pale yellow syrup separated which soon solidified; the acid crystallised from benzene in pale yellow cubes, m. p. 117—118°. The reduction of this acid to 2 : 4 : 6-trimethylmandelic acid, $C_6H_2Me_3\cdot CH(OH)\cdot CO_2H$, by sodium amalgam was first carried out by Feith (*Ber.*, 1891, **24**, 3545), but, in order to see whether more vigorous reduction would lead to the formation of 2 : 4 : 6-trimethylphenylacetic acid, $C_6H_2Me_3\cdot CH_2\cdot CO_2H$ (compare the reduction of dimethylterephthalonic acid, p. 2434), mesitylglyoxylic acid was dissolved in sodium carbonate and boiled with a large excess of sodium amalgam (3%) for 4 hours. The acid obtained on the addition of hydrochloric acid crystallised from water in brilliant cubes, m. p. 152—154°, and consisted of trimethylmandelic acid (Found: C = 67·8; H = 7·2. $C_{11}H_{14}O_3$ requires C = 68·0; H = 7·2%). There was no indication of the formation of trimethylphenylacetic acid. When mesitylglyoxylic acid is oxidised by permanganate, it yields dimethylterephthalonic acid as the main product.

*Dimethylterephthalonic Acid* (III).—The second and third fractions of the calcium salts, on dissolving in dilute hydrochloric acid and allowing to cool, yielded almost colourless crystals containing some mesitylglyoxylic acid, which was readily removed by extraction with hot benzene. The residue was crystallised from water, from which dimethylterephthalonic acid separated in pale yellow prisms, m. p. 220°. No loss occurred on drying on the steam-bath (Found: C = 59·8; H = 4·7. $C_{11}H_{10}O_5$ requires C = 59·5; H = 4·5%). This acid is rather sparingly soluble in cold but readily soluble in hot water; it combines with sodium hydrogen sulphite, but the solution of this derivative does not lose carbon dioxide on boiling

with the formation of the aldehydo-acid as is the case with phthalonic acid (Graebe and Trumpy, *Ber.*, 1898, **31**, 375).

The *dimethyl* ester was first obtained by boiling the acid with excess of thionyl chloride for an hour, distilling off the excess under reduced pressure, decomposing the residue by boiling with methyl alcohol, and then precipitating with water. It may also be prepared by boiling the acid (5 g.) with methyl alcohol (50 c.c.) and concentrated sulphuric acid (10 c.c.) for an hour and then diluting with water. The oil which is precipitated in either case, soon crystallises and, after washing with sodium carbonate, the dimethyl ester separates from methyl alcohol in prisms or from light petroleum in stars of needles, m. p. 85° (Found: C = 62·5; H = 5·7. $C_{13}H_{14}O_5$ requires C = 62·4; H = 5·6%).

Terephthalonic acid is decomposed when its solution in concentrated sulphuric acid is heated on the steam-bath, carbon monoxide is disengaged, and, on diluting with water, the solution deposits 2 : 6-dimethylterephthalic acid which, after crystallisation from alcohol, melts at 297—298°.

When the boiling aqueous solution of dimethylterephthalonic acid is heated with phenylhydrazine (1 mol.) on the steam-bath, the *phenylhydrazone* is deposited as a red-brown mass which separates with difficulty from alcohol in rather indefinite crystals, m. p. 213° (decomp.) (Found: N = 8·7. $C_{17}H_{16}O_4N_2$ requires N = 9·0%).

*Oxidation.* The dilute solution of the acid, neutralised with potassium carbonate and cooled to 0°, was gradually mixed with the calculated quantity of 1% permanganate, a stream of carbon dioxide being passed the whole time. The filtrate from the manganese precipitate was concentrated, acidified, and the precipitate crystallised from alcohol, from which 2 : 6-dimethylterephthalic acid separated in microscopic needles, m. p. 296—298° (Found: C = 61·9; H = 5·3. $C_{10}H_{10}O_4$ requires C = 61·8; H = 5·1%).

*Reduction of Dimethylterephthalonic Acid.*—(1) *4-Carboxy-2 : 6-dimethylmandelic acid* (p. 2429). The acid, dissolved in dilute sodium carbonate, was reduced below 15° with excess of powdered 3% sodium amalgam; after 24 hours the filtered solution was acidified with hydrochloric acid, the voluminous precipitate collected, washed, and crystallised from boiling water, when the mandelic acid separated as a mass of crystals which, under the microscope, were seen to be thin plates made up of needles. The air-dried substance seems to contain 1 aq, since it lost 7·5% on heating at 115°, whereas $C_{11}H_{12}O_5,H_2O$ contains $H_2O$ = 7·4%. Found, in substance dried at 115°: C = 58·9; H = 5·6. $C_{11}H_{12}O_5$ requires C = 58·9; H = 5·6%). *Carboxydimethylmandelic acid* softens at 230° and melts at 243—244° with effervescence; it is rather sparingly

soluble in cold water or benzene, but readily soluble in methyl alcohol. When the acid is heated at 250°, it effervesces with loss of steam, but not of carbon dioxide and yields a very viscid syrup which sets to a brittle resin, lactide formation apparently taking place. The resin dissolves readily in boiling aqueous sodium carbonate, and hydrochloric acid precipitates from the cooled solution a mass like gelatinous silica; on boiling, this becomes crystalline, melts at about 235—242° (decomp.), and appears to be the mandelic acid.

(II) 4-*Carboxy*-2 : 6-*dimethylphenylacetic acid* (p. 2429). Reduction to this acid takes place when dimethylterephthalonic acid, dissolved in boiling dilute sodium carbonate, is reduced at the boiling temperature with a large excess of sodium amalgam (3%) for several hours. The product is made nearly neutral with hydrochloric acid, filtered, and acidified hot, when an immediate separation of a colourless acid occurs which is very sparingly soluble even in boiling water. This was collected, extracted with boiling water to remove any of the mandelic acid (see above), and crystallised from 50% acetic acid, from which the acid separates in microscopic groups of flat prisms (Found : in substance dried at 120° : C = 63·5; H = 6·1. $C_{11}H_{12}O_4$ requires C = 63·5; H = 5·8%).

4-*Carboxy*-2 ; 6-*dimethylphenylacetic acid*, m. p. about 285° (without decomp.), is readily soluble in methyl alcohol, but sparingly soluble in benzene; it dissolves in much boiling water and separates, on cooling, as a chalky precipitate consisting of microscopic, striated leaflets.

The *dimethyl* ester, $C_6H_2Me_2(CO_2Me)\cdot CH_2\cdot CO_2Me$.—This characteristic derivative was obtained by boiling the acid with excess of thionyl chloride for an hour, evaporating off the excess, and decomposing the solid acid chloride with methyl alcohol. After adding water, the viscid syrup was extracted with ether, the extract well washed with sodium carbonate, dried, and evaporated. The residual syrup soon crystallised, and the solid separated from light petroleum in thick, colourless prisms, m. p. 78° (Found : C = 65·9; H = 6·9. $C_{13}H_{16}O_4$ requires C = 66·1; H = 6·8%). This dimethyl ester is very readily soluble in ether or benzene, sparingly soluble in cold light petroleum, readily soluble on boiling, and separates, on cooling, in characteristic stars of prisms.

4-*Carboxy*-2 : 6-*dimethylbenzaldehyde* (XIII).—When dimethylterephthalonic acid (10 g.), dissolved in boiling water, is heated with aniline (9 c.c.) on the steam-bath, the clear solution begins to crystallise after about ½ hour and the substance which separates (B) is sparingly soluble in alcohol and crystallises in colourless rhombs, m. p. 168°, is readily soluble in sodium carbonate with

separation of aniline, and is evidently the *aniline* salt of *anilodimethylterephthalonic acid* (XI) (Found: C = 70·7; H = 5·8; N = 7·0. $C_{23}H_{22}O_4N_2$ requires C = 70·8; H = 5·6; N = 7·2%). If this substance is boiled with sodium carbonate for a few minutes, the liberated aniline extracted with ether, and the well-cooled solution acidified, a sticky precipitate separates which soon hardens and evidently consists of anilodimethylterephthalonic acid, since the solution in methyl alcohol, in which it is very readily soluble, on the addition of aniline and heating to boiling, immediately deposits the aniline salt, m. p. 168°.

When the mother-liquor from (B) is heated for several hours on the steam-bath and allowed to cool, a further considerable crop of crystals is obtained and this substance is very readily soluble in alcohol and separates from methyl alcohol as a crust of lemon-yellow needles, m. p. 185—186° (Found: C = 76·2; H = 6·1; N = 5·6. $C_{16}H_{15}O_2N$ requires C = 75·9; H = 5·9; N = 5·5%). This substance is therefore *anilo-4-carboxy-2 : 6-dimethylbenzaldehyde* (XII), produced by the elimination of aniline and carbon dioxide from the aniline salt (B); it is also produced when the aniline salt is boiled with xylene for an hour and separates on cooling in yellow needles. This substance is readily soluble in acetone or ether and dissolves immediately in cold dilute sodium carbonate. It is readily soluble in boiling benzene, from which it crystallises in stars of needles and flat plates, and these appear to be dimorphic modifications, because, on standing and stirring, the needles change into the plates. The hydrolysis of the anilo-derivative to the aldehyde was carried out by boiling with moderately concentrated hydrochloric acid for an hour, during which the lemon-yellow substance did not dissolve but became colourless. The precipitate was collected, thoroughly washed to remove all traces of aniline hydrochloride, dissolved in sodium carbonate, filtered from a trace of insoluble matter, and acidified with hydrochloric acid. Finally, the *4-carboxy-2 : 6-dimethylbenzaldehyde* was crystallised from alcohol, in which it is rather sparingly soluble and from which it separates in colourless needles, m. p. 211—212° (Found: C = 67·6; H = 5·7. $C_{10}H_{10}O_3$ requires C = 67·4; N = 5·6%). The *phenylhydrazone* was obtained by adding a slight excess of phenylhydrazine to the boiling aqueous solution of the aldehydo-acid; the yellow precipitate crystallised from methyl alcohol in lemon-yellow needles, m. p. about 228° (Found: N = 10·5. $C_{16}H_{16}O_2N_2$ requires N = 10·4%).

*4 : 6-Dimethylphthalonic acid* (IV).—The mother-liquor from the decomposition of the crude calcium dimethylterephthalonate by hydrochloric acid (p. 2432), as well as the mother-liquors from the

recrystallisation of this acid and of crude mesitylglyoxylic acid, contains a small amount of the above acid, and, on concentrating under reduced pressure and adding concentrated hydrochloric acid, this separates as a syrup which gradually crystallises. After several fractional crystallisations from dilute hydrochloric acid, small, colourless crystals were obtained which melted at 178° and consisted of *anhydrous* 4 : 6-dimethylphthalonic acid (Found: C = 59·4; H = 4·7. $C_{11}H_{10}O_5$ requires C = 59·5; H = 4·5%. 0·1714 neutralised 15·5 c.c. of *N*/10-NaOH; *M* = 221. $C_{11}H_{10}O_5$ requires *M* = 222). When the supersaturated solution of the acid, in water alone, is allowed to stand, it gradually deposits large four-sided prisms, m. p. 86—87°, which consist of the *hydrated* acid, $C_6H_2Me_2(CO_2H)\cdot C(OH)_2\cdot CO_2H$ (Found: in air-dried substance, C = 54·6; H = 5·1. $C_{11}H_{12}O_6$ requires C = 55·0; H = 5·0%). The molecule of water is readily lost on heating on the steam-bath, and the fused mass soon solidifies; m. p. 175—176°. Moreover, when a small quantity of hydrochloric acid is added to the supersaturated aqueous solution of the hydrated acid, the anhydrous acid separates on cooling.

The *dimethyl* ester, obtained by digesting the acid with excess of thionyl chloride for an hour, evaporating away the excess, and boiling the residue with methyl alcohol, separates from methyl alcohol (70%) in colourless needles, m. p. 76—79° (Found : C = 61·9; H = 5·8. $C_{13}H_{14}O_5$ requires C = 62·4; H = 5·6%).

The constitution of this acid was proved by heating with concentrated sulphuric acid on the steam-bath, when carbon monoxide was eliminated and, on pouring into water, a chalky precipitate was deposited which crystallised from alcohol in needles, m. p. 115°, of 4 : 6-dimethylphthalic anhydride. This anhydride gave the fluorescein reaction; on hydrolysis with dilute sodium hydroxide and then acidification with hydrochloric acid, 4 : 5-dimethylphthalic acid was deposited in colourless needles, m. p. 185—186°.

*Action of aniline.* An aqueous solution of 4 : 6-dimethylphthalonic acid was heated with aniline (2 mols.) on the steam-bath for several hours, during which colourless crystals separated, and these crystallised from methyl alcohol in needles, m. p. 213°. Analysis showed that this substance is the *anilide* of *anilo-2-carboxy-4 : 6-dimethylbenzaldehyde* (XIV) (Found : C = 80·6; H = 6·3; N = 8·3. $C_{22}H_{20}ON_2$ requires C = 80·5; H = 6·1; N = 8·5%). In the hope of obtaining the aldehydo-acid, this substance was heated on the steam-bath with moderately concentrated hydrochloric acid for several hours, when it did not pass completely into solution, but was converted into a substance which separated from methyl alcohol in colourless, hexagonal plates, m. p. 174°. As this substance does

not dissolve in cold dilute sodium carbonate, it is clearly the *anilide* of *2-carboxy*-4 : 6-*dimethylbenzaldehyde* (XV) (Found : C = 75·9; H = 6·0. $C_{16}H_{15}O_2N$ requires C = 75·9; H = 5·9%).

*Methylcarboxyphthalonic Acid* (V or Va).—The isolation of small quantities of this very deliquescent acid is described on p. 2431. When exposed to air, it is rapidly converted into a paste, and all attempts to recrystallise it were unsuccessful. After drying at 100°, it melted at about 218° (decomp.), the analytical results agreed approximately with the formula $C_{11}H_8O_7$, which was confirmed by titration, when 0·1113 neutralised 13·1 c.c. of *N*/10-NaOH (*M* = 253. $C_{11}H_8O_7$ requires *M* = 252). A substance which is evidently the dimethyl ester of this acid is described on p. 2432, and reference is also made to the trimethyl ester on p. 2432. Definite proof of the composition of this acid was obtained by the study of its behaviour on reduction. The acid, dissolved in water and neutralised with sodium hydroxide, was reduced by a large excess of sodium amalgam (2½%) on the steam-bath, and the filtered solution acidified with hydrochloric acid, when a solid separated which crystallised from water in microscopic plates, m. p. 228°, and is evidently *methyldicarboxymandelic acid*,

$$C_6H_2Me(CO_2H)_2{\cdot}CH(OH){\cdot}CO_2H$$

(Found : C = 51·9; H = 4·2. $C_{11}H_{10}O_7$ requires C = 52·0; H = 3·9%). This acid does not deliquesce when exposed to air.

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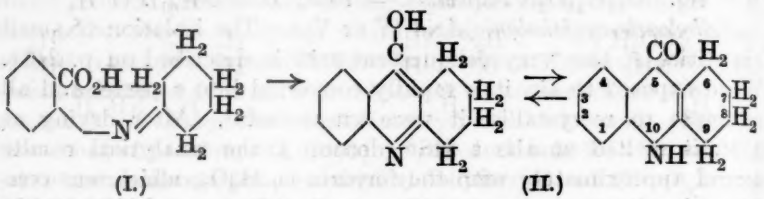
## CCCXXXIII.—*Tetrahydroacridine, Octahydroacridine, and their Derivatives.*

By WILLIAM HENRY PERKIN, jun., and WILLIAM GREENWELL SEDGWICK.

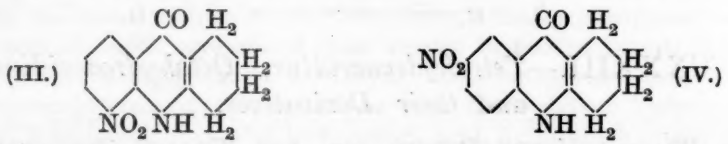
THE probability that strychnine and brucine contain the reduced nuclei both of acridine and carbazole has made it desirable that the reduction products of these substances should be studied in various directions, and the objects of the present investigation have been (i) to study the general behaviour of the reduced acridine skeleton, and (ii) to determine whether partly reduced acridines and acridones are capable of yielding additive derivatives with nitric acid in the way that derivatives of tetrahydrocarbazole have been shown to do (Perkin and Plant, J., 1923, **123**, 678). Tiedtke (*Ber.*, 1909, **42**, 625) found that *cyclo*hexylideneanthranilic acid (I) is obtained when anthranilic acid is heated with *cyclo*hexanone at 120° and that, at

220°, further elimination of water takes place with the formation of tetrahydroacridone (II) (compare Graebe and Lagodzinski,



(I.) (II.)

*Annalen*, 1893, **276**, 47). The addition of four atoms of hydrogen to one benzene nucleus in acridone results in a marked increase in basicity, since tetrahydroacridone yields definite salts with strong mineral acids whereas acridone itself is almost devoid of basic properties. Tiedtke (*loc. cit.*) has pointed out that tetrahydroacridone, although stable under ordinary conditions, is oxidised to acridone when sublimed in contact with air and we find that the same change takes place on heating with sulphuric acid. We have been unable to obtain any indication of the formation of an additive derivative on treating tetrahydroacridone with nitric acid under a variety of conditions. The product in all cases was the nitrate which, on account of its sparing solubility, made additive experiments difficult to carry out. When the base, in solution in concentrated sulphuric acid, is treated with nitric acid, it yields two mononitro-derivatives melting at 227° (III) and 336° (IV), respectively, the structures of which have been demonstrated by synthesis.

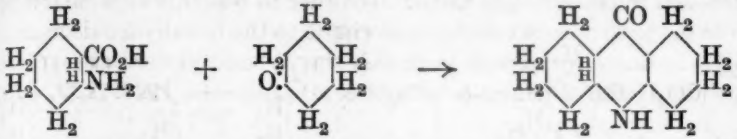


(III.) (IV.)

1-*Nitrotetrahydroacridone* (III) was obtained from 3-nitroanthranilic acid by condensation with *cyclo*hexanone, and 3-*nitrotetrahydroacridone* (IV) in a similar manner from 5-nitroanthranilic acid. The series of the nitrotetrahydroacridones was also completed by the synthesis of the 4- and 2-isomerides (m. p. 270° and 332°, respectively).

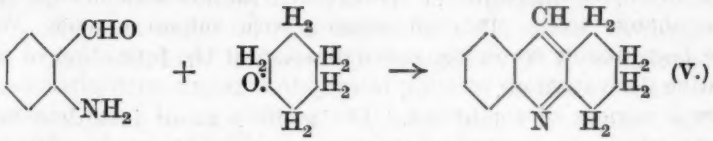
These nitro-derivatives are bright yellow substances very sparingly soluble in organic solvents, but readily soluble in hot aqueous and especially alcoholic potassium hydroxide to red solutions. On treatment with acid reducing agents, they are reduced to the corresponding *aminotetrahydroacridones* without any addition of hydrogen to the double linking and the amino-derivatives diazotise normally and yield characteristic *acetyl* derivatives.

*Decahydroacridone* was synthesised by heating together hexahydroanthranilic acid and *cyclo*hexanone :

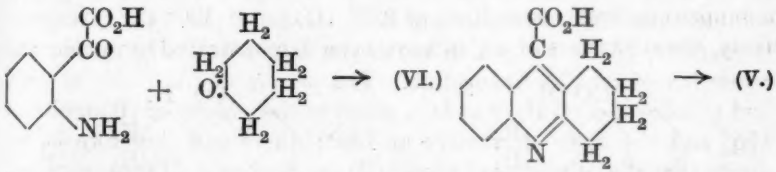


It melts at 275° and is a strong base; attempts to reduce this electrolytically to the completely hydrogenated acridine ring were not successful, a substance melting at 180° was obtained which appeared to have the composition $C_{13}H_{21}ON$, but its nature was not determined.

In order to study tetrahydroacridine itself (V), we prepared this substance in our first experiment by the method of Borsche (*Ber.*, 1908, **41**, 2206), which consists in condensing *o*-aminobenzaldehyde with *cyclo*hexanone, but the more convenient process is to condense



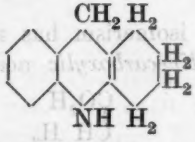
isatin with *cyclo*hexanone in alkaline solution and to heat the tetrahydroacridinecarboxylic acid (VI) so produced (yield 80%),

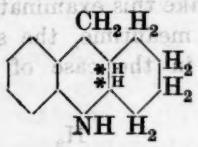


when it loses carbon dioxide and is quantitatively converted into tetrahydroacridine (Borsche, *loc. cit.*). Experiments on the action of nitric acid on tetrahydroacridine were made under a variety of conditions, but in no case was addition of ·OH and ·$NO_2$ to the double linking observed. When the solution of the base in sulphuric acid is treated with nitric acid, it is converted into a *nitrotetrahydroacridine* which is probably the 4-nitro-derivative, but the determination of the position of the nitro-group has not been found possible, because we were unsuccessful in our attempts to reduce the nitro-derivative to 4-aminooctahydroacridine, the properties of which are known (p. 2447).

Since the addition of ·OH and ·$NO_2$ or ·OH and ·OH to the double linking in tetrahydrocarbazole has been observed only in the case of the action of nitric acid on the 9-benzoyl or 9-acetyl derivative,

it was thought that its non-occurrence in the case of tetrahydroacridine might possibly be due to the absence of an acid radical attached to the nitrogen atom. In order to test this view, attempts were made to reduce tetrahydroacridine to the hexahydro-derivative (VII) in order to prepare from this the *N*-benzoyl derivative corresponding with 9-benzoyltetrahydrocarbazole (J., 1923, **123**, 678).

(VII.) 

 (VIII.)

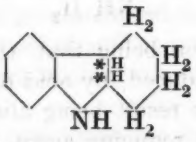
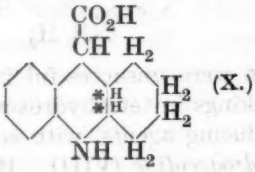
We were unsuccessful in this, the reason being that the double linkings in tetrahydroacridine (V) are reduced, by acid or alkaline reducing agents, with equal facility, the result being always *octahydroacridine* (VIII). If the amount of reducing agent employed is only sufficient to supply two atoms of hydrogen, then the product consists of a mixture of octahydroacridine with unchanged tetrahydroacridine. This behaviour may be taken as evidence in favour of formula (V) as the correct representation of the constitution of tetrahydroacridine.

The octahydroacridine obtained in the manner just described is always a mixture of two isomerides, namely (A) m. p. 82°, and (B) m. p. 72°, and these are readily separated by taking advantage of the fact that the sulphate and picrate of (A) are less readily soluble than the corresponding derivatives of (B). Of these two isomerides, (A) is formed in much the larger quantity during the reduction of tetrahydroacridine. The *picrate* of (A) melts at 195° and the *acetyl* derivative at 86°, whereas the *picrate* of (B) melts at 175° and the *acetyl* derivative at 136°; there can therefore be no doubt that the substances (A) and (B) are distinct. If the structural formula of octahydroacridine (VIII) be examined, it will be seen that the substance possesses two asymmetric carbon atoms (marked *) which are not similarly environed, as in the tartaric acids, so that the *meso*-possibility is excluded. It can therefore exist in two modifications each potentially resolvable into optically active constituents. The well-defined substances (A) and (B) are presumably these two racemic modifications and the attempt will be made to resolve them. A case of this kind has not, so far as we are aware, been previously recorded,* but it may be pointed out that hexahydrocarbazole (IX) also contains two asymmetric carbon atoms and should therefore occur in two resolvable modifications, but, so

* This case is, of course, distinct from that of decahydronaphthalene which, according to Huckel (*Diss.*, Göttingen), exists in two stereoisomeric modifications.

far, only one modification, melting at 99°, has been isolated. This modification is readily obtained when tetrahydrocarbazole is reduced by tin and hydrochloric acid or electrolytically (Perkin and Plant, this vol., p. 1512), but the mother-liquors from its recrystallisation, which may contain the second isomeride only in small quantity, do not appear to have been systematically examined and we propose to undertake this examination.

In the meantime, the same kind of isomerism has also been observed in the case of *octahydroacridinecarboxylic acid* (X).

(IX.)  (X.) 

When tetrahydroacridinecarboxylic acid (VI) is reduced by sodium amalgam, the product is a mixture of two octahydroacridinecarboxylic acids, (A and B), which again should be capable of resolution.

The acid (A) melts at 180° and when heated at about 260° is decomposed quantitatively into (A) octahydroacridine (m. p. 82°). The isomeric acid (B) melts at 221° and also decomposes at 260° with elimination of carbon dioxide and formation of (B) octahydroacridine (m. p. 72°). We propose to attempt the resolution of these isomeric octahydroacridinecarboxylic acids.

The octahydroacridines are very stable substances and show no tendency to oxidise in the air, in direct contrast with the ease with which dihydroacridine changes, on exposure, to acridine (Graebe and Caro, *loc. cit.*). The further reduction of the octahydroacridines to tesserakaidecahydroacridine by alkaline or acid agents or electrolytically has been attempted, but without success. The stability of the benzene nucleus in the octahydroacridines must be greatly enhanced by the reduced system to which it is attached and Willstätter (*Ber.*, 1923, **56**, 1388) has observed a similar phenomenon in the case of the reduction of naphthalene. Naphthalene is readily converted by hydrogen, in presence of spongy platinum poor in oxygen, into decahydronaphthalene, $C_{10}H_{18}$, but the further reduction of tetrahydronaphthalene, $C_{10}H_{12}$, to $C_{10}H_{18}$ is a more difficult matter and proceeds much more slowly.

## Experimental.

*Tetrahydroacridone* (II).—This substance was prepared from anthranilic acid and *cyclo*hexanone essentially under the conditions recommended by Tiedtke (*Ber.*, 1909, **42**, 624). The crude tetrahydroacridone thus obtained is a grey-white, crystalline mass,

m. p. about 357°; it may be recrystallised from alcohol, but is sufficiently pure for most preparative work. The *nitrate*, prepared (1) by rubbing the base with 5% nitric acid until it formed a paste and then collecting, washing, and recrystallising from alcohol, (2) by adding nitric acid (1 mol.) to the solution of tetrahydroacridone in glacial acetic acid, separating immediately as a crystalline precipitate (Found: C = 59·5; H = 5·3; N = 10·5. $C_{13}H_{13}ON,HNO_3$ requires C = 59·5; H = 5·3; N = 10·6%) crystallises from alcohol in glistening plates; when gradually heated it yields a crystalline sublimate of nitrotetrahydroacridone (see below). The *hydrochloride* was obtained by dissolving the base in warm concentrated hydrochloric acid and cooling in ice, when the liquid set to a crystalline mass which was drained on porous tile. It crystallises from alcohol in colourless needles.

*Methyltetrahydroacridone* (6- or 8-).—This substance was prepared from 1-methyl*cyclo*hexan-3-one and anthranilic acid exactly as described in the case of tetrahydroacridone, which it closely resembles in appearance and properties. The first product of the interaction—3-*methyl*cyclo*hexylideneanthranilic acid*—separates from benzene in plates, m. p. 140° (Found: N = 6·2. $C_{14}H_{17}O_2N$ requires N = 6·1%). On heating at 220°, this acid yielded methyltetrahydroacridone, which crystallises from alcohol in needles, m. p. 342° (with darkening). Only one of the two possible isomerides was produced in this way.

*Methyl* 3-*methyl*cyclo*hexylideneanthranilate* was obtained by heating methyl anthranilate (2 g.) with *cyclo*hexanone for 2 hours at 120°. The liquid product was treated at 0° with concentrated hydrochloric acid, the sparingly soluble hydrochloride of the ester collected, decomposed by ice-cold alkali, and the methyl ester extracted with ether. It is a yellow syrup which cannot be distilled under reduced pressure and, when hydrolysed by boiling with dilute acid, it yields anthranilic acid and *cyclo*hexanone.

3-*Nitro*- and 1-*Nitro-tetrahydroacridone*.—Tetrahydroacridone (10 g.), dissolved in concentrated sulphuric acid (70 c.c.), was cooled to — 15° and the theoretical quantity of powdered potassium nitrate (5 g.) added in small quantities, the solution being continuously stirred and kept at — 10°. The product was poured on to ice, the crude yellow mixture of nitro-derivatives collected, washed with water, then with alcohol, and dried in a vacuum over sulphuric acid. The dry mass was extracted with boiling alcohol, the red alcoholic solution (A) filtered off, and the residue, which is about 95% of the whole, crystallised from equal volumes of alcohol and hydrochloric acid, from which the 3-nitro-derivative separates in thick, rectangular prisms, m. p. 336° (decomp.) (Found: C = 63·8;

H = 5·0; N = 11·6. $C_{13}H_{12}O_3N_2$ requires C = 63·9; H = 4·9; N = 11·5%). The alcoholic filtrate (A) deposited, on cooling, needles of the 1-nitro-derivative and, on recrystallisation from alcohol, this separated in orange-yellow needles in contrast to the bright yellow crystals of the 3-nitro-derivative. M. p. 227° (Found: C = 63·9; H = 5·1; N = 11·5%).

*Synthesis of* 3-*Nitrotetrahydroacridone.*—5-Nitroacetylanthranilic acid was prepared by nitrating acetylanthranilic acid (Rupe, *Ber.*, 1897, **30**, 1097) and converted into 5-nitroanthranilic acid by careful hydrolysis.

Owing to the ready elimination of the carboxyl group, the yield of this acid is small and the best results were obtained by heating the acetyl derivative with alcoholic hydrochloric acid or a mixture of glacial acetic acid (3 parts) and sulphuric acid (1 part) diluted with an equal volume of water. The acid separated from boiling water in dark red needles, m. p. 263° (decomposition). This 5-nitro-acid (1 g.) and *cyclo*hexanone (1 g.) were heated together at 120° for 2 hours, when, on cooling, cyclo*hexylidene*-5-*nitroanthranilic acid* separated; it crystallised from alcohol in red needles, m. p. 271° (decomposition) (Found: N = 10·6. $C_{13}H_{14}O_4N_2$ requires N = 10·7%). In the preparation of 3-nitrotetrahydroacridone, this intermediate stage was not isolated, but the mixture, after heating at 120°, was gradually heated to 220° and maintained at this temperature until the reaction was complete. The solid product was extracted with a little alcohol to remove the coloured impurity, and the residue crystallised from alcoholic hydrochloric acid (Found: N = 11·6. $C_{13}H_{12}O_3N_2$ requires N = 11·5%). This 3-nitrotetrahydroacridone melted at 336° and was found to be identical with the substance of the same melting point obtained by the direct nitration of tetrahydroacridone.

*Synthesis of* 1-*Nitrotetrahydroacridone.*—Part of the 3-nitro-anthranilic acid used in this experiment was prepared from 3-nitro-salicylic acid (Hübner, *Annalen.*, 1879, **195**, 37), but most of it from 3-nitrophthalic anhydride (Bogert and Boroschek, *J. Amer. Chem. Soc.*, 1901, **23**, 746) by converting this into 3-nitrophthalamidic acid and treating with sodium hypochlorite in place of the hypo-bromite recommended by Kahn (*Ber.*, 1902, **35**, 3863); the yield is nearly quantitative. This nitro-acid was heated with *cyclo*-hexanone under the conditions described in detail in the case of the synthesis of the 3-nitro-derivative, except that the temperature was not allowed to exceed 180°. After crystallisation from alcohol, the product melted at 227° and proved to be identical with the 1-nitro-derivative obtained in the direct nitration of tetrahydro-acridone.

*Synthesis of 2-Nitrotetrahydroacridone.*—4-Nitroanthranilic acid was prepared by nitrating *o*-toluidine (Nölting and Collin, *Ber.*, 1884, **17**, 265), acetylating the resulting 4-nitro-*o*-toluidine, and oxidising the acetonitrotoluidide with neutral permanganate (Wheeler, *J. Amer. Chem. Soc.*, 1898, **20**, 221). If the oxidation is carried out at 80° and the acetyl derivative then hydrolysed with alcoholic hydrochloric acid, the nitro-acid is obtained in almost quantitative yield; it separates from alcohol in bright yellow needles, m. p. 264°. cyclo*Hexylidene-4-nitroanthranilic acid*, prepared by heating 4-nitroanthranilic acid (1 g.) with *cyclo*hexanone (1 g.) at 140° for 2 hours, separated from alcohol in yellow needles, m. p. 269° (decomp.).

In preparing 2-nitrotetrahydroacridone, this acid was not isolated but the temperature of the mixture was gradually raised to 220° and the residue, after grinding and washing with hot alcohol, recrystallised from alcoholic hydrochloric acid from which 2-nitrotetrahydroacridone separated in bright yellow needles, m. p. 332° (Found: N = 11·0. $C_{13}H_{12}O_3N_2$ requires N = 11·5%).

*Synthesis of 4-Nitrotetrahydroacridone.*—Equal quantities of 6-nitroanthranilic acid (Bogert and Chambers, *J. Amer. Chem. Soc.*, 1905, **27**, 744) and *cyclo*hexanone were heated for 2 hours at 120°, during which a yellow, crystalline mass separated. The whole was mixed with ether, the crystalline precipitate washed with alcohol and analysed (Found: N = 10·8. $C_{13}H_{14}O_4N_2$ requires N = 10·7%.

6-*Nitro*cyclo*hexylideneanthranilic acid* melts at about 214° with decomposition and, on standing in the air, slowly changes and the melting point falls. It is decomposed on boiling with alcohol (97%) or with water or dilute acids into 6-nitroanthranilic acid and *cyclo*hexanone. In preparing 4-nitrotetrahydroacridone, this acid was not isolated, but the mixture of 6-nitroanthranilic acid and *cyclo*hexanone was heated for 1 hour at 120°, the temperature gradually raised to 210° and, when effervescence had ceased, to 220° for an hour. The dark residue was extracted several times with boiling benzene, dissolved in alcoholic hydrochloric acid, and gradually precipitated with water. The crystalline mass of 4-nitrotetrahydroacridone, so obtained, is very sparingly soluble in the usual solvents and melts at about 270°.

3-*Aminotetrahydroacridone.*—3-Nitrotetrahydroacridone was dissolved in the minimum amount of boiling alcoholic hydrochloric acid and zinc dust gradually added, when the colour disappeared during the course of an hour. After the solution had been filtered and concentrated, the *hydrochloride* of the base separated in glistening plates, m. p. 310° (with darkening), readily soluble in alcohol or water. The base was obtained by dissolving the hydrochloride in

a little water and carefully neutralising with ammonia, when a crystalline precipitate immediately separated and this crystallised from alcohol in long needles, m. p. 322° (with darkening). The alcoholic solution exhibits a blue fluorescence (Found: C = 72·7; H = 6·6; N = 12·3. $C_{13}H_{14}ON_2$ requires C = 72·9; H = 6·5; N = 13·0%). The *acetyl* derivative was prepared by heating the base with acetic anhydride on the steam-bath for an hour and separated from glacial acetic acid in prisms, m. p. 344° (with darkening) (Found: C = 70·0; H = 6·2. $C_{15}H_{16}O_2N_2$ requires C = 70·3; H = 6·2%).

1-*Aminotetrahydroacridone*, prepared by the reduction of the 1-nitro-derivative by means of zinc dust and alcoholic hydrochloric acid exactly as described in the case of the 3-amino-derivative, separates from ether in rosettes of prisms, m. p. 255° (with darkening) (Found: N = 12·9. $C_{13}H_{14}ON_2$ requires N = 13·0%).

2-*Aminotetrahydroacridone* was prepared in a similar manner and also by the reduction of 2-nitrotetrahydroacridone, dissolved in alcoholic hydrochloric acid, with stannous chloride (Found: C = 73·0; H = 6·7. $C_{13}H_{14}ON_2$ requires C = 72·9; H = 6·5%). The *hydrochloride*, which is rather sparingly soluble and crystallises in needles, was decomposed by ammonia and the base crystallised from alcohol, from which it separated in silky needles, m. p. about 320° (with darkening). The *acetyl* derivative crystallises in rectangular plates, m. p. 336° (Found: C = 70·1; H = 6·4. $C_{15}H_{16}O_2N_2$ requires C = 70·3; H = 6·2%).

*Decahydroacridone.*—Hexahydroanthranilic acid (5 g.), prepared by the reduction of anthranilic acid with sodium and *iso*amyl alcohol, was thoroughly mixed with *cyclo*hexanone (5 g.), the mixture heated at 130° for 2 hours and then at 260° for a further 2 hours, during which some of the decahydroacridone sublimed into the condenser. The mass was extracted with hot water to remove unchanged acid, and crystallised from alcohol, from which it separated in glistening, rectangular plates or prisms, m. p. 275° (with darkening) (Found: C = 76·1; H = 9·4; N = 6·8. $C_{13}H_{19}ON$ requires C = 76·1; H = 9·3; N = 6·8%). Decahydroacridone is readily soluble in dilute hydrochloric acid and the nitrate and sulphate are sparingly soluble; it does not yield a characteristic picrate. Attempts to reduce this base electrolytically yielded a substance which distilled at 190°/10 mm. and partially crystallised. After being washed with ether, the crystals melted at 179—180°, and gave C = 74·0; H = 10·5, whereas $C_{13}H_{21}ON$ requires C = 75·4; H = 10·1, but the amount of material was too small for further investigation.

*Tetrahydroacridine* (V).

Tetrahydroacridinecarboxylic acid (VI) was made by the condensation of isatin with *cyclo*hexanone in presence of alcoholic potassium hydroxide essentially under the conditions recommended by Borsche (*Ber.*, 1908, **41**, 2207), and recrystallised from alcohol, from which it separated in yellow needles, m. p. 285°. The acid was heated, in quantities of 10 grams, in a small distillation flask at 290° and, when the evolution of carbon dioxide had ceased, the residue was distilled under 10 mm., when it passed over at about 150° and solidified immediately (6·5 g.; m. p. 53°); after recrystallisation from petroleum, the *tetrahydroacridine* melted at 54·5°.

The *sulphate* was obtained, in long, slender needles, on cooling a warm concentrated solution of the base in dilute sulphuric acid, and after crystallisation from alcohol melted at 220°. The *nitrate* was prepared by dissolving the base in warm dilute nitric acid, when the salt immediately crystallised; it separated from alcohol in pale yellow plates, m. p. 160° (Found: N = 11·0. $C_{13}H_{13}N,HNO_3$ requires N = 11·3%).

The *picrate*, m. p. 208° (decomp.), is readily obtained by mixing a hot alcoholic solution of the base with hot alcoholic picric acid. *Tetrahydroacridine methoiodide*, prepared by heating the base (2 g.) with methyl iodide (4 g.) in ethereal solution for 2 hours, crystallises from a mixture of ether and alcohol in needles, m. p. 202—204°.

5-*Chlorotetrahydroacridine*.—Tetrahydroacridone (2 g.) was mixed with phosphorus pentachloride (2·2 g.), sufficient phosphoryl chloride added to make a thin paste, and the whole gradually heated at 120° and kept at this temperature until the bulk of the oxychloride had distilled over. Ice and water were added, when the chloro-derivative dissolved as the hydrochloride, and, on adding ammonia, the base separated; it crystallised from alcohol in colourless prisms melting at 226° to a green liquid (Found: Cl = 15·9. $C_{13}H_{12}NCl$ requires Cl = 16·3%). The chloro-derivative dissolves in most organic solvents, yielding green solutions from which it separates in colourless crystals. It is a strong base and the solutions in dilute mineral acids exhibit a green fluorescence. The *hydrochloride*, obtained by allowing the solution of the base in dilute hydrochloric acid to concentrate at the ordinary temperature, crystallises in colourless needles and is very soluble in water. On boiling with dilute acids, chlorotetrahydroacridine is gradually converted into tetrahydroacridone.

(4 ?)-*Nitrotetrahydroacridine* is readily obtained when tetrahydroacridine (2 g.), dissolved in boiling glacial acetic acid (6 c.c.), is mixed with nitric acid (1·6 c.c.); on allowing to cool, some of the

nitro-derivative crystallises out and the rest is obtained by diluting with water and adding excess of ammonia. The same substance is obtained by dissolving tetrahydroacridine (5 g.) in concentrated sulphuric acid (50 c.c.) and slowly stirring in powdered potassium nitrate (1·1 g.), water and ammonia are then added, and the nitro-derivative crystallised from alcohol, from which it separates in orange brown needles, m. p. 110° (Found : N = 12·2. $C_{13}H_{12}O_2N_2$ requires N = 12·3%).

(4 ?)-*Aminotetrahydroacridine.*—The nitro-derivative (2 g.), dissolved in the minimum of hot alcohol, was mixed with stannous chloride (6 g.) dissolved in concentrated hydrochloric acid (10 c.c.), and left to stand over-night, when most of the aminotetrahydro-acridine had separated as the sparingly soluble hydrochloride. The hydrochloride was ground with concentrated aqueous ammonia, the base collected, washed, and recrystallised from ether or aqueous alcohol, from which it separated in needles, m. p. 160° (Found : C = 78·4; H = 7·2; N = 13·9. $C_{13}H_{14}N_2$ requires C = 78·8; H = 7·1; N = 14·1%). Aminotetrahydroacridine yields yellow salts with mineral acids and of these the *hydrochloride* (feathery, orange needles, m. p. 242°) and the *nitrate* are sparingly soluble. The *picrate* is obtained by adding picric acid to the boiling alcoholic solution of the base or its hydrochloride and separates, on cooling slowly, in stout, red prisms, m. p. 236° (decomp.).

The *acetyl* derivative was obtained by adding acetic anhydride (0·9 c.c.) to the saturated alcoholic solution of the base (1 g.) and heating to boiling. On the addition of a little water, it separated in elongated prisms, m. p. 204° (Found : C = 75·2; H = 6·7. $C_{15}H_{16}ON_2$ requires C = 75·0; H = 6·7%). When boiled with concentrated hydrochloric acid, this acetyl derivative is readily hydrolysed and, on cooling, the hydrochloride of the base separates.

(4 ?)-*Amino-octahydroacridine.*—The reduction of the nitrotetra-hydroacridine to the corresponding amino-derivative of octahydro-acridine may be accomplished by means of acid reducing agents, but the isolation of the base is difficult owing to its ready oxidisability.

Nitrotetrahydroacridine (2 g.), dissolved in concentrated hydro-chloric acid (25 c.c.), was gently boiled with tin (6 g.) for 12 hours, the solution diluted, filtered, and the dissolved tin removed by hydrogen sulphide. The base was then precipitated by a slight deficiency of ammonia, so that the solution remained slightly acid. The colourless ethereal extract of the base rapidly darkened and the *acetyl* derivative was therefore prepared by adding acetic anhydride (1 c.c.) to the carefully dried ethereal solution and evaporating slowly on the steam-bath. The solid residue crystallised from alcohol in colourless needles, m. p. 195°, but the yield was poor

(Found: C = 73·4; H = 8·4. $C_{15}H_{20}ON_2$ requires C = 73·8; H = 8·2%).

The *hydrochloride* of the base may be obtained by passing hydrogen chloride into the dry ethereal solution and is precipitated as a colourless, granular mass, m. p. 235°, which is readily soluble in water and slowly reddens on exposure to the air. The aqueous solution diazotises normally and yields, with an alkaline solution of β-naphthol, a deep red precipitate.

*The Octahydroacridines* (VIII) *and Octahydroacridinecarboxylic Acids* (X).

1. *Reduction of Tetrahydroacridine.*—A solution of the base (5 g.) in alcohol (20 c.c.) and concentrated hydrochloric acid (35 c.c.) was boiled with tin (5 g.) for 12 hours, the alcohol distilled off under reduced pressure, the residual liquid mixed with a large excess of potassium hydroxide (40%), and several times extracted with ether. The syrup obtained from the extract (dried with potassium carbonate) rapidly solidified and separated from petroleum in indefinite crystals, m. p. about 30—50°. It is possible, by repeated fractional crystallisation from light petroleum, to isolate from this mixture of (A) and (B) nearly pure octahydroacridine (B), but the process is wasteful and completely satisfactory separation may be achieved by using either of the methods (*a*) or (*b*):

(*a*) The mixed bases (4 g.) are gradually added to sulphuric acid (30 c.c. of 50%) at 50°, the whole well stirred, and just sufficient hot water added to dissolve the sulphates. On remaining overnight, the sulphate of (A) will have separated almost completely and, after recrystallisation from water, this is decomposed by alkali and the base crystallised from light petroleum, from which it separates in large plates, m. p. 81—82° (Found: C = 83·0; H = 9·0, $C_{13}H_{17}N$ requires C = 83·4; H = 9·1%).

(*b*) The mixed bases (4 g.), dissolved in hot alcohol (20 c.c.), are mixed with a hot solution of picric acid (4·9 g.) in the minimum of alcohol, and the sparingly soluble picrate is immediately collected. After recrystallisation from much alcohol, this melts at 195° and when decomposed by ammonia and extracted with ether, yields the base (A), which, after recrystallisation from light petroleum, melts at 82°.

The picrate which is deposited on cooling the first alcoholic filtrate, can be separated into the picrates of (A) and (B, m. p. 175°) by repeated recrystallisation. The picrate of (B), on decomposition with ammonia and recrystallisation of the precipitate from ligroin (after extraction with ether), yields the pure base (B), m. p. 72°.

II. *Reduction of Tetrahydroacridone.*—In an apparatus provided

with an efficient stirrer, the substance (5 g.), dissolved in alcohol (250 c.c.), was mixed with sodium bicarbonate, heated at 80°, and then sodium amalgam (125 g. of 4%) gradually added, carbon dioxide being passed during the whole time. After heating and stirring for 6 hours, the solution was filtered, the filtrate evaporated to dryness under reduced pressure, the residue extracted with ether and dried over potassium carbonate. After removal of ether, the residue distilled at 160°/10 mm., solidified, and separated from light petroleum in plates, m. p. 82°. This isomeride seems to be the only product of this reduction and if (B) is formed at all it must be in very small quantity (Found: C = 83·0; H = 9·0. $C_{13}H_{17}N$ requires C = 83·4; H = 9·1%). *Octahydroacridine* (A) melts at 82° and is characterised by the sparing solubility of its *sulphate* in water and of the *picrate* (m. p. 195°) in alcohol. It dissolves readily in dilute mineral acids and the addition of sodium nitrite to the dilute solution of the hydrochloride at 0°, causes a sparingly soluble nitroso-derivative to separate. The *methoiodide*, prepared by boiling the solution of the base in ether with methyl iodide, crystallises from alcohol–ether in pale yellow prisms, m. p. about 212°. The *acetyl* derivative was obtained by boiling the base with acetic anhydride (3 parts) for 2 hours and decomposing with ice, when an oil separated which soon solidified and crystallised from light petroleum in colourless plates, m. p. 86° (Found: C = 78·5; H = 8·7. $C_{15}H_{19}ON$ requires C = 78·6; H = 8·3%). This acetyl derivative is readily hydrolysed by boiling with alcoholic potassium hydroxide with regeneration of the base, m. p. 82°.

10-*Methyloctahydroacridine* (A).—A solution of the base (2 g.) in acetone (10 c.c.) was well stirred with methyl sulphate (4 g.) and sodium hydroxide (6 c.c. of 40%) at 50°, the acetone distilled off, and the residue extracted with ether. From the extract, dried over potassium carbonate, an oil was obtained, b. p. 140°, which did not crystallise (Found: C = 83·5; H = 9·4. $C_{14}H_{19}N$ requires C = 83·6; H = 9·5%).

This substance is readily soluble in dilute mineral acids; the *picrate*, obtained by adding hot alcoholic picric acid to the alcoholic solution of the base, separates in thick prisms and melts at 160° to a green solution. When tetrahydroacridine methoiodide (p. 2446) is reduced with sodium amalgam in the manner described above, a base is obtained which yields a picrate melting, after recrystallisation, at 160°, and from this, by decomposition with ammonia, 10-methyloctahydroacridine (A) is obtained. In both the above experiments, search was made for the picrate of the 10-methyl derivative of (B), but without success.

(4 ?)-*Nitro-octahydroacridine* (A).—Octahydroacridine (A) cannot

be directly nitrated, but the nitro-derivative may be obtained from the acetyl derivative as follows: The acetyl derivative (2 g.) is dissolved in concentrated sulphuric acid (20 c.c.), and powdered potassium nitrate (0·9 g.) gradually added with stirring. The product is poured on to ice, the yellow solid collected, dissolved in alcohol, and boiled for 45 minutes with concentrated hydrochloric acid (2·5 c.c.); the *hydrochloride* of nitro-octahydroacridine, which crystallises on cooling, separates from alcohol in rectangular plates, m. p. 198° (Found: C = 58·3; H = 6·7. $C_{13}H_{16}O_2N_2$,HCl requires C = 58·1; H = 6·3%).

Nitro-octahydroacridine (A) separates, on adding ammonia to the alcoholic solution of the hydrochloride, in red needles, m. p. 104°, after recrystallisation (Found: C = 67·2; H = 7·0. $C_{13}H_{16}O_2N_2$ requires C = 67·2; H = 6·9%). The alcoholic hydrochloric acid mother-liquor contains the hydrochloride of a second nitro-derivative, and the base separates from alcohol in yellow needles, m. p. 180° (Found: C = 67·6; H = 7·0%).

*Octahydroacridine* (B).—The readily soluble sulphate of this base is contained in the mother-liquors of the sulphate of the base (A) (p. 2448).

After as much as possible of the sparingly soluble sulphate has been removed, the solution is made alkaline with sodium hydroxide, the base extracted with ether, and repeatedly recrystallised from light petroleum, from which it separates in plates, m. p. 72°.

The same base is also obtained from the picrate melting at 175 (p. 2448) by decomposing with ammonia and extracting with ether (Found: C = 83·0; H = 9·0. $C_{13}H_{17}N$ requires C = 83·4; H = 9·1%).

The *methiodide*, prepared by digesting the ethereal solution of the base with methyl iodide, crystallises in pale yellow prisms, m. p. 217° (Found: C = 51·2; H = 6·3. $C_{14}H_{20}NI$ requires C = 51·1; H = 6·1%).

The *acetyl* derivative, prepared by boiling the base with acetic anhydride, crystallises well from alcohol in prisms, m. p. 136°, and yields the base (B) on hydrolysis with alcoholic potassium hydroxide (Found: C = 78·4; H = 8·4. $C_{15}H_{19}ON$ requires C = 78·6; H = 8·3%).

*Octahydroacridinecarboxylic Acid* (A).—A mixture of this acid with the isomeride (B) is obtained when tetrahydroacridinecarboxylic acid (p. 2446; 10 g.), dissolved in sodium hydroxide, is reduced by the gradual addition of sodium amalgam (200 g. of 4%), at first in the cold and finally for 3 hours at 85°, a current of carbon dioxide being passed the whole time. On acidifying the filtered solution with acetic acid, the mixed acids separate as a white, crystalline

mass and, on fractionally crystallising from alcohol, the more sparingly soluble acid (A) is readily obtained pure in colourless needles, melting without decomposition at 180° (Found : C = 72·5; H = 7·2. $C_{14}H_{17}O_2N$ requires C = 72·7; H = 7·3%).

When this acid is heated at 260°, it decomposes with liberation of carbon dioxide; the residue distils at 160°/10 mm., crystallises from light petroleum in plates, m. p. 82°, and consists of octahydroacridine (A).

*Octahydroacridinecarboxylic acid* (B) is obtained from the mother-liquors of (A), by repeated fractional crystallisation from alcohol, in colourless plates, melting at 221° without change. (Found : C = 72·9; H = 6·8%). When this acid is heated at 260°, it decomposes with liberation of carbon dioxide and formation of octahydroacridine (B) which, after distillation under reduced pressure and crystallisation from light petroleum, melts at 72° and at the same temperature when mixed with a specimen of (B) obtained by the reduction of tetrahydroacridine (p. 2448).

One of us (W. G. S.) desires to express his thanks to the Salters' Research Institute for a grant which has enabled him to take part in this investigation. We are indebted to Mr. T. V. Barker for advice in considering the stereoisomerism of the octahydroacridines and to Mr. F. Hall for carrying out many of the analyses.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, August 12th,* 1924.]

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## CCCXXXIV.—*Derivatives of Acridone and Tetrahydrocarbazole.*

By WILFRED HERBERT LINNELL and WILLIAM HENRY PERKIN, jun.

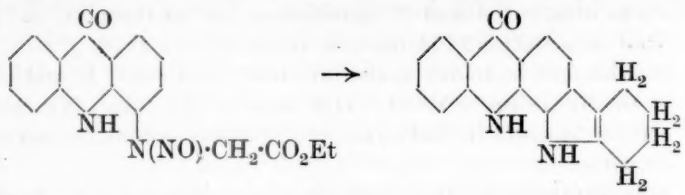
ONE of the most remarkable changes in the strychnine and brucine group is the decomposition of brucinolic acid into glycollic acid and brucinolone,

$$C_{23}H_{26}O_8N_2 + H_2O = C_2H_4O_3 + C_{21}H_{22}O_5N_2 + H_2O,$$

a change which takes place readily on boiling with dilute alkali (Leuchs and Weber, *Ber.*, 1909, **42**, 771). These investigators suggest that this decomposition is due to the hydrolysis of the grouping $>N{\cdot}CH_2{\cdot}CO_2H$ into $>NH$ and $CH_2(OH){\cdot}CO_2H$ by the addition of a molecule of water.

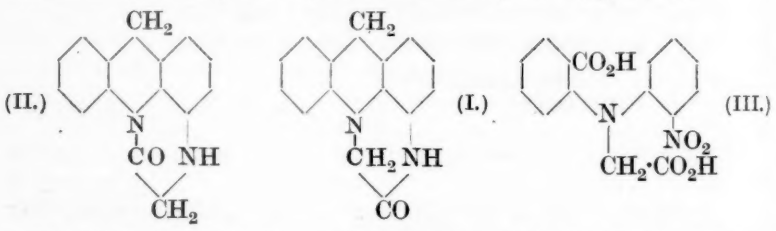
A case somewhat similar to this was met with during the course of synthetical experiments in the strychnine and brucine series (Clemo, Perkin, and Robinson, this vol., p. 1753). It was found

that the nitroso-derivative of acridone-9-aminoacetic ester, when treated with zinc dust and acetic acid in presence of *cyclo*hexanone,



yields 5-keto-5 : 10 : 16 : 17 : 18 : 19-hexahydroacrindoline,* the $-CH_2 \cdot CO_2Et$ group in the former being eliminated during the process.

This curious elimination of the acetic residue from the grouping $>N \cdot CH_2 \cdot CO_2H$ is clearly a matter of importance, owing to its bearing on the question of the constitution of strychnine, brucine, and their derivatives, and one of the main objects of the present investigation has been to find other examples of this change and to determine under what conditions it takes place. The first case met with was in attempting to prepare anhydro-9-aminodihydroacridine-10-acetic acid (I), a substance of interest on account of its isomerism with the anhydrodihydroacridine-9-aminoacetic acid (II) obtained by Clemo, Perkin, and Robinson (*loc. cit.*, p. 1760).



The first step was to prepare 6-carboxy-2′-nitrodiphenylamine-*N*-acetic acid (III), which it was thought would result from the condensation of phenylglycine-*o*-carboxylic acid,

$$C_6H_4(CO_2H) \cdot NH \cdot CH_2 \cdot CO_2H,$$

with *o*-chloronitrobenzene in presence of copper as the catalyst.

The substance produced under these conditions is, however, 2′-nitrodiphenylamine-6-carboxylic acid (C. P. & R., *loc. cit.*, p. 1752), elimination of the acetic residue having taken place during the condensation.

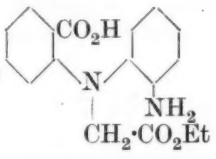
That this decomposition is not due to the combined weights of the groups attached to the nitrogen atom is shown by the fact that the half-ester of the acid (III) is readily obtained when 2′-nitrodiphenylamine-6-carboxylic acid is digested with bromoacetic ester. This substance is soluble in sodium carbonate and is reprecipitated

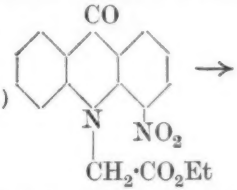
* For the system of nomenclature, compare C. P. & R. (*loc. cit.*, p. 1769).

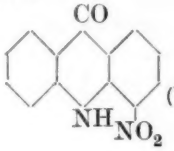
by acids, but when the attempt was made to hydrolyse it by boiling with very dilute potassium hydroxide (1 per cent.), the $-CH_2 \cdot CO_2Et$ group was eliminated and 2′-nitrodiphenylamine-6-carboxylic acid separated on acidifying. A possible reason for the ready removal of this group might be found in the proximity of the $CO_2H$ and $-NO_2$ groups to the group $>N \cdot CH_2 \cdot CO_2H$ and, if this were the correct explanation, it seemed likely that the stability would be increased if the nitro-group were reduced to the amino-group. In order to test this supposition, the nitro-ester was reduced by stannous chloride to *6-carboxy-2′-aminodiphenylamine-N-acetic ester* (IV), an oil which yields a crystalline acetyl derivative,

$$CO_2H \cdot C_6H_4 \cdot N(CH_2 \cdot CO_2Et) \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3.$$

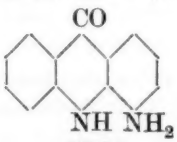
This substance was then hydrolysed by dilute alkali, but again the acetic residue was removed and the product obtained on acidifying was 2′-aminodiphenylamine-6-carboxylic acid. A series of experiments was then made in the hope of converting the half-ester of the acid (III) into 9-nitroacridone-10-acetic ester (V) by treatment with dehydrating agents, but in this case also, the acetic residue was eliminated and the product was 9-nitroacridone (VI).

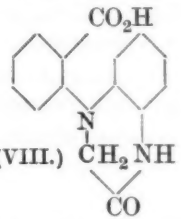
(IV.) 

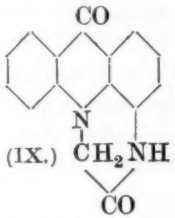
(V.) 


(VI.)

Experiments made with the object of obtaining the anhydro-derivative (VIII) or (IX) from the amino-ester (IV) by treatment with sulphuric acid were unsuccessful. In this case again, the acetic acid residue was eliminated and the product isolated was 9-aminoacridone (VII). It was also observed that even saturating


(VII.)

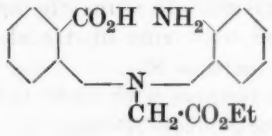

(VIII.)

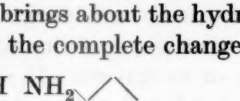

(IX.)

the solution of the amino-ester (IV) in methyl alcohol with hydrogen chloride causes decomposition, and acetic ester and the ester of 2′-aminodiphenylamine-6-carboxylic acid are obtained.

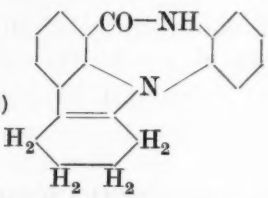
Lastly, the action of heat alone on 6-carboxy-2′-aminodiphenylamine-*N*-acetic ester (IV) was investigated and it was found that, under reduced pressure, this substance decomposes on heating

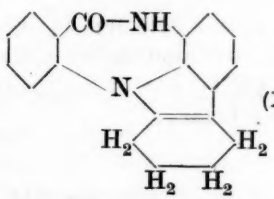
gently and glycollic acid solidifies in the receiver. The residue in the distillation flask is anhydro-2′-aminodiphenylamine-6-carboxylic acid (X), which Clemo, Perkin, and Robinson (*loc. cit.*, p. 1779) had already obtained by the action of heat on the acid itself. It is evidently the water liberated in the formation of this anhydro-derivative which brings about the hydrolysis, and the elimination of glycollic acid and the complete change may be represented thus :

(IV.)  $+ H_2O =$

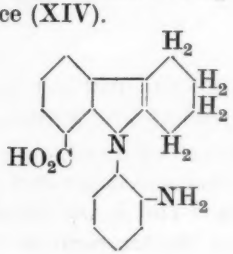
(X.)  $+ \begin{matrix} CH_2 \cdot OH \\ | \\ CO_2H \end{matrix} + Et \cdot OH$

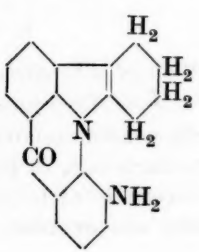
In possession of considerable quantities of anhydro-2′-aminodiphenylamine-6-carboxylic acid, we have more completely examined its properties than was possible on the former occasion. The nitroso-derivative, when reduced with zinc dust and acetic acid in presence of *cyclo*hexanone yields, almost quantitatively, a tetrahydrocarbazole derivative, the constitution of which might be represented either by (XI) or (XII).

(XI.) 

 (XII.)

The decision in favour of (XI) was obtained in the following way. On hydrolysis with alcoholic potassium hydroxide the anhydro-linking, $-NH \cdot CO-$, becomes hydrolysed and the resulting amino-acid must be 2′-amino-9-phenyl-1 : 2 : 3 : 4 :-tetrahydrocarbazole-8-carboxylic acid (XIII), because, on treatment with sulphuric acid, acridone ring closure takes place evidently with the formation of the substance (XIV).

(XIII.) 

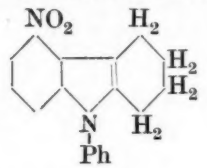
 (XIV.)

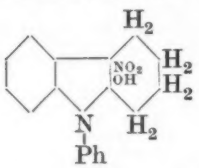
This seems to prove that the original condensation product must be the anhydro-derivative of the acid (XIII), because a substance of the formula (XII) could hardly yield an acridone on hydrolysis and subsequent treatment with sulphuric acid.

The parent substance, 9-*phenyltetrahydrocarbazole*, has not been described and, as we were desirous of studying its properties, and especially its behaviour on reduction, we have prepared it and submitted it to a preliminary investigation. It is readily obtained when nitrosodiphenylamine is reduced with zinc dust and acetic acid in presence of *cyclo*hexanone and melts at 86°.

It is interesting that this substance behaves with nitric acid in a similar manner to 9-benzoyltetrahydrocarbazole (Perkin and Plant, J., 1923, **123**, 675), that is to say, part of it is simply nitrated with the formation of a substance which is probably 5-*nitro*-9-*phenyltetrahydrocarbazole* (XV), but the main portion adds on ·OH and ·$NO_2$ at the unsaturated linking of the tetrahydro-ring and yields 11-*nitro*-10-*hydroxy*-9-*phenylhexahydrocarbazole* (XVI).

(XV.)

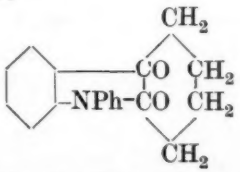



(XVI.)

When this substance is heated with potassium hydroxide, it is readily decomposed with the formation of o-*anilinobenzoylvaleric acid* (XVII), the decomposition evidently taking place according to the scheme:

(XVI.) →

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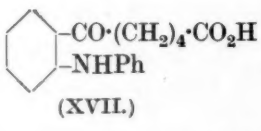


(XVII.)

a change which, it will be observed, is analogous to that which 11-nitro-9-benzoyl-10-hexahydrocarbazole undergoes under similar conditions (Perkin and Plant, *loc. cit.*).

## EXPERIMENTAL.

*Condensation of Phenylglycine-o-carboxylic Acid with* o-*Chloronitrobenzene. Formation of 2′-Nitrodiphenylamine-6-carboxylic Acid.*

Phenylglycine-*o*-carboxylic acid (5 g.), *o*-chloronitrobenzene (6 g.), potassium carbonate (3 g.), and copper-bronze powder (0·2 g.) were heated together with efficient stirring. The mass liquefied at 110°, water was evolved, and, on raising the temperature to 160°,

solidification took place after about 2 hours. Heating was continued for a further hour, after which a little water was added and the excess of *o*-chloronitrobenzene removed by steam distillation, animal charcoal being added towards the end of this operation. After filtering, acidification with acetic acid precipitated a dark red solid which, crystallised from alcohol, melted at 216°, alone or mixed with 2′-nitrodiphenylamine-6-carboxylic acid.

This reaction was repeated under less vigorous conditions, *i.e.*, refluxing the reactants in (*a*) amyl alcohol, (*b*) in toluene, (*c*) in benzene for 3 hours, but in every case the same product was obtained.

*Ethyl 6-Carboxy-2′-nitrodiphenylamine-N-acetate.*—A mixture of 2′-nitrodiphenylamine-6-carboxylic acid (2 g.) in the minimum amount of absolute alcohol, bromoacetic ester (2 g.), and potassium acetate (2 g.) was gently refluxed for 10 hours. It was then filtered, diluted with water, allowed to cool, and acidified with acetic acid, when a dark red, semi-solid mass separated which could be crystallised from alcohol, or better from light petroleum (b. p. 60—80°), from which it separated in pale orange, elongated prisms, m. p. 74·5° after recrystallisation (Found : C = 59·1; H = 4·5; N = 8·1. $C_{17}H_{16}O_6N_2$ requires C = 59·3; H = 4·6; N = 8·1%). The substance dissolves with difficulty in sodium carbonate, more readily in ammonia, and easily in sodium hydroxide and is reprecipitated on acidification with acetic acid.

*Action of potassium hydroxide.* The ester (1 g.) was gently refluxed with 50 c.c. of 10% methyl-alcoholic potassium hydroxide for 3 hours. On pouring into water and acidifying with acetic acid, a yellow precipitate was obtained which melted at 215° and proved to be 2′-nitrodiphenylamine-6-carboxylic acid, since there was no depression on mixing these substances. The same result was obtained when 1% aqueous or methyl-alcoholic potassium hydroxide was used.

All attempts to convert the nitro-ester into 9-nitroacridone-10-acetic ester (V) were unsuccessful. The methods employed with this object in view may be summarised thus :

| Method. | Product. |
|---|---|
| Heating on a steam-bath with concentrated sulphuric acid. | 9-Nitroacridone. |
| Treating with thionyl chloride and subsequent refluxing with aluminium chloride in toluene. | 9-Nitroacridone. |
| Phosphoric oxide in xylene. | A tar. |
| Phosphoryl chloride in toluene. | 9-Nitroacridone. |
| Refluxing with acetic anhydride and fused potassium acetate. | Material unchanged. |

*Ethyl 6-Carboxy-2′-aminodiphenylamine-N-acetate* (IV).—The reduction of the nitro-ester may be effected by the use of ferrous

sulphate and ammonia or zinc and alcoholic hydrochloric acid, but the best yield was obtained as follows :

The ester (3 g.) was dissolved in the minimum amount of ether, to which was added the calculated quantity of a 20% solution of stannous chloride in ether saturated with hydrogen chloride. The colour of the solution immediately changed from orange to a dark yellowish-brown and, after 2 hours, the sides of the flask became coated with grey, crystalline cubes of the double compound of stannic chloride with the amino-ester. Excess of 30% sodium hydroxide was added, the whole extracted with ether, and, on evaporation of the solvent, the crude amino-ester remained as a pale yellow syrup which did not crystallise. This was dissolved in ether (30 c.c.), mixed with a slight excess of acetic anhydride, and, after 1 hour, an equal bulk of water was added and the ether evaporated, when a yellow oil separated which immediately solidified to a rubber-like mass. Crystallised from benzene or dilute acetic acid, *ethyl 6-carboxy-2′-acetylaminodiphenylamine-N-acetate* was obtained in long, colourless needles, m. p. 121° (Found : C = 64·0; H = 5·6; N = 7·8. $C_{19}H_{20}O_5N_2$ requires C = 64·0; H = 5·6; N = 7·9%). All attempts to obtain the pure amino-ester from this acetyl derivative were unsuccessful.

*Hydrolysis.* The crude amino-ester (3 g.) was refluxed with 30 c.c. of 10% methyl-alcoholic potassium hydroxide for 3 hours. On pouring into water, a red solution was obtained which, on acidification with acetic acid, gave a reddish-yellow precipitate. After two crystallisations from xylene, this substance melted at 212°, alone or mixed with 2′-aminodiphenylamine-6-carboxylic acid (Found : C = 68·6; H = 5·1. Calc., C = 68·4; H = 5·3%).

The same result was obtained with 1% methyl-alcoholic or aqueous potash.

In attempting the conversion of the amino-ester into 9-amino-acridone-10-acetic acid or its anhydro-derivative (IX) the following methods were employed without success.

| Method. | Product. |
|---|---|
| Solution of the amino-ester in methyl alcohol saturated with hydrogen chloride, (*a*) left over-night, (*b*) left over-night and then gently refluxed for 5 hours. | Methyl ester of 2′-aminodiphenylamine-6-carboxylic acid, m. p. 86°. |
| Heating on a steam-bath with concentrated sulphuric acid. | 9-Aminoacridone. |
| Treatment with thionyl chloride, and subsequently with aluminium chloride in toluene. | 9-Aminoacridone. |
| Phosphoric oxide in xylene. | A tar. |
| Phosphoryl chloride in toluene. | A tar. |
| Refluxing with acetic anhydride and fused potassium acetate. | Material unchanged. |

Having failed to obtain 6-carboxy-2′-aminodiphenylamine-*N*-acetic ester in crystalline form, it was thought that distillation might produce the desired result. An attempt was therefore made to distil the amino-ester (10 g.) under reduced pressure (10 mm.). At a bath temperature of 200°, a small quantity of a distillate was obtained which solidified on keeping. This substance crystallised from hot water or ether, melted at 80°, and proved to be glycollic acid, since it showed no depression of melting point when mixed with this acid. No further distillation took place, even on heating at 350°, and the residue in the flask solidified to a green, crystalline mass, which, when crystallised from aqueous pyridine, melted at 250° and proved to be anhydro-2′-aminodiphenylamine-6-carboxylic acid (X).

*Anhydro-2′-amino-9-phenyltetrahydrocarbazole-8-carboxylic Acid* (XI).—Anhydro-2′-aminodiphenylamine-6-carboxylic acid, prepared by following the directions of Clemo, Perkin, and Robinson (*loc. cit.*, p. 1779), was heated at 250° for 10 minutes, when water was eliminated and the anhydro-derivative obtained in a crude crystalline form. This was recrystallised twice from aqueous pyridine and the nitroso-compound formed in the usual way, care being taken that the temperature did not rise above 5° during the reaction. The nitroso-derivative (5 g.), *cyclo*hexanone (5 g.), and zinc dust (12·5 g. of 98%) were suspended in alcohol (25 c.c.), to which was added, in the space of 1 hour, with efficient cooling and stirring, 50 c.c. of glacial acetic acid. The whole was filtered with suction, the residue washed with a little alcohol, and the filtrate heated at 65—70° for 1 hour. After the mixture had been cooled and poured on to ice, the green precipitate which separated was collected, washed with a little water, and crystallised from 60% acetic acid, from which it was obtained in large, well-defined, elongated prisms, m. p. 204° (Found : C = 79·1 ; H = 5·3 ; N = 9·5. $C_{19}H_{16}ON_2$ requires C = 79·2 ; H = 5·6 ; N = 9·7%).

*Hydrolysis.* The anhydro-derivative (5 g.) was boiled for 15 minutes with potassium hydroxide (3 g.) dissolved in water (10 c.c.) and alcohol (30 c.c.), and after cooling and diluting with water, the clear solution was acidified with acetic acid. The *2′-amino-9-phenyltetrahydrocarbazole-8-carboxylic acid* which separated, crystallised with difficulty from dilute alcohol and melted at 168° (Found : C = 74·8 ; H = 5·7 ; N = 9·6. $C_{19}H_{18}O_2N_2$ requires C = 74·5 ; H = 5·9 ; N = 9·1%).

The diazonium salt, when coupled with β-naphthol, gave a red dye, thus proving the presence of the primary amino-group. When the acid (2 g.) was heated on a steam-bath for 15 minutes with concentrated sulphuric acid (14 g.) and diluted with ice and water, a

dirty white precipitate was obtained which crystallised from boiling xylene or nitrobenzene and melted at 262°. This substance, when mixed with anhydro-2′-amino-9-phenyltetrahydrocarbazole-8-carboxylic acid, showed a depression of melting point, and also responded to the tests for a primary amine. Thus, although it has the same empirical composition as the above anhydro-derivative, there is no doubt that the substances are not identical (Found: C = 79·1; H = 5·4; N = 9·2. $C_{19}H_{16}ON_2$ requires C = 79·2; H = 5·6; N = 9·7%).

9-*Phenyltetrahydrocarbazole.*—Nitrosodiphenylamine (15 g.) and zinc dust (35 g.) are suspended in alcohol (100 c.c.) containing 15 g. of *cyclo*hexanone. Glacial acetic acid (100 c.c.) is then gradually added during 1 hour, the mixture being efficiently stirred throughout and the temperature, which tends to rise considerably, kept below 10° by cooling in ice and salt. The mixture is filtered, the zinc residues washed with a little alcohol, the filtrate heated at 65—70° for 1 hour, and, after being allowed to cool, poured on to ice. The precipitate is collected, washed, and dried. It crystallises from methyl alcohol in large, almost colourless, elongated prisms, m. p. 86° (Found: C = 87·3; H = 6·9; N = 5·5. $C_{18}H_{17}N$ requires C = 87·4; H = 6·9; N = 5·6%).

*Action of nitric acid.* 9-Phenyltetrahydrocarbazole (10 g.) was dissolved in glacial acetic acid (20 c.c.), nitric acid (*d.* 1·4; 5 g.). diluted with a little acetic acid, gradually added while the mixture was efficiently stirred and the temperature kept at 40°. Considerable darkening took place, but no crystallisation was noticed, and after the stirring had been continued for 3 hours, a little water was added, when a semi-solid, partly crystalline mass (8·5 g.) separated. This crystallised from dilute acetic acid in almost colourless needles, m. p. 145° (decomp.) and proved to be 11-*nitro*-10-*hydroxy*-9-*phenylhexahydrocarbazole* (XVI) (Found: C = 69·6; H = 5·8; N = 9·0. $C_{18}H_{18}O_3N_2$ requires C = 69·7; H = 5·8; N = 9·0%).

The acetic acid mother-liquors from this substance yielded, on further dilution with much water, a yellow mass (0·7 g.), which, after two crystallisations from methyl alcohol, was obtained in bright yellow plates, m. p. 120° and proved to be 5(?)-*nitro*-9-*phenyltetrahydrocarbazole* (XV) (Found: C = 74·0; H = 5·4; N = 9·4. $C_{18}H_{16}O_2N_2$ requires C = 73·9; H = 5·5; N = 9·6%).

o-*Anilinobenzoylvaleric acid* (XVII).—11-Nitro-10-hydroxy-9-phenylhexahydrocarbazole (6 g.) was heated for 15 minutes with potassium hydroxide (12 g.) dissolved in water (80 c.c.) and alcohol (150 c.c.) and, after cooling and diluting with water, the clear solution was acidified with acetic acid, when an oil separated which, on standing and rubbing, solidified. The acid separated from weak alcohol

in colourless needles, m. p. 92° (Found: C = 72·3; H = 6·4; N = 4·7. $C_{18}H_{19}O_3N$ requires C = 72·7; H = 6·4; N = 4·7%).

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THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, August 12th*, 1924.]

## CCCXXXV.—*Studies in the Organic Polysulphides. Part III. The Action of the Disulphides of the Alkali Metals and of Sodium Tetrasulphide on some Organic Halogen Compounds.*

By JOHN SMEATH THOMAS and RICHARD WILLIAM RIDING.

LEAVING out of account the rare rubidium and cæsium compounds, it has been shown by Thomas and Rule (J., 1917, **111**, 1063) and Thomas and Jones (this vol., p. 2207) that, although other unstable polysulphides may exist, the only stable compounds of the alkali metals are the disulphides, the tetrasulphide of sodium, and the pentasulphides of potassium and ammonium. The reactions of such of these compounds as have not already been dealt with in previous papers of this series, when they are treated with organic halogen derivatives, form the subject of this communication.

Ammonium pentasulphide appears to react in a similar manner to potassium pentasulphide, giving rise in all cases to pentasulphides of the radicals examined in excellent yield.

The behaviour of the disulphides of sodium and lithium (Thomas and Jones, *loc. cit.*) was studied. In both cases an organic disulphide was produced. The reaction proceeds smoothly but rather slowly. But for this disadvantage pure organic disulphides could most conveniently be prepared in this way.

Disulphides of various organic radicals have already been described, notably by Spring and Demarteau (*Bull. Soc. chim.*, 1889, [iii], **1**, 314), Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 81), Holmberg (*Annalen*, 1908, **359**, 81), and Price and Twiss (J., 1907, **91**, 2021). The properties of the disulphides now obtained conform to the descriptions of these compounds given by those authors and no further account of them is necessary. It may be pointed out, however, that no evidence could be obtained of the presence of thio-ethers in any of the specimens of disulphides examined in the course of this work.

Now, if the inorganic polysulphides have the structure $R_2S{:}S$

advocated by Küster and Heberlein (*Z. anorg. Chem.*, 1905, **43**, 72) and Holmberg (*loc. cit.*), the reaction under discussion should result, at any rate to some extent, in the formation of organic disulphides of the same constitution, from the decomposition of which thioethers would be obtained. Moreover, since organic disulphides are produced by the oxidation of mercaptans, into which they are reconverted by reduction, they must have the constitution R·S·S·R. These disulphides are identical with those obtained by the authors and it is not unreasonable to suppose, therefore, that the inorganic disulphides are similarly constituted. This is in accordance with the view previously expressed by Thomas and Rule (*loc. cit.*) on other grounds.

Sodium tetrasulphide reacts with organic halogen compounds in a somewhat remarkable manner. In no case was a tetrasulphide obtained, the final product being invariably a mixture of pentasulphide and disulphide, formed, apparently, in accordance with the equations

$$Na_2S_4 + 2RI \longrightarrow R_2S_4 + 2NaI.$$
$$3R_2S_4 \longrightarrow 2R_2S_5 + R_2S_2.$$

This observation is obviously of considerable importance from the point of view of the structure to be assigned to polysulphides. Any theory of the constitution of these compounds must provide an explanation of this phenomenon. This question will be fully discussed in a future communication.

In many respects the resemblance between the organic polysulphides and the polysulphides of the alkali metals is very close. In every case investigated, a disulphide has been shown to exist, and this appears to be the most stable compound of the series. The higher stable compound obtained by the method of preparation employed was always the pentasulphide, no matter which alkali polysulphide, other than the disulphide, was used.

It may be pointed out here that a study of the absorption spectra of these compounds does not support Holmberg's contention (*loc. cit.*) that the pronounced difference between the colours of the organic polysulphides and those of the polysulphides of the alkali metals indicates that the two classes are constituted differently.

In discussing the absorption spectra of the organic pentasulphides, dibenzyl pentasulphide may be taken as a typical example, for it is the organic polysulphide most readily obtained in a high degree of purity. Solutions of this substance in alcohol, alcohol containing a little sodium ethoxide (deep yellow), alcohol and ammonia (colourless), and in piperidine (deep red) were examined. General absorption was observed in each case. Solutions of potassium penta-

sulphide and of sodium tetrasulphide in alcohol also exhibit general absorption.

Now, in the case of substances showing general absorption in the visible region, a band might exist in the ultra-violet and the more nearly this band approached the visible region the more intense would be the colour of the substance. It is clear, therefore, that the difference in colour does not necessarily indicate a difference in structure, but, rather, that in the case of the organic compounds the force fields are more condensed.

In the investigation of the reaction between sodium tetrasulphide and organic halogen derivatives advantage was taken of the volatility of the disulphide in order to separate the crude oily product into its constituents. In the earlier experiments, the oil was distilled under atmospheric pressure until all the disulphide had been removed. Later, this procedure was modified and the disulphide was removed by evaporation below 80° in a vacuum. In both cases, the result was the same. The non-volatile residue, which was soluble in ether and in pentane, was found to be the pentasulphide.

Even at this low temperature, however, it seemed possible that the pentasulphide might be formed by a gradual decomposition of the tetrasulphide and that this change did not take place at the moment of formation, as was supposed. In order to decide between these possibilities, the crude oil obtained by the interaction of sodium tetrasulphide with propyl bromide was kept in a vacuum over phosphoric oxide at the laboratory temperature, and the percentage of sulphur in the oil was periodically determined. The results obtained are given in Table I.

TABLE I.

| Time (days) ..... | 0 | 9 | 18 | 38 | 74 |
|---|---|---|---|---|---|
| S % ..... | 56·53 | 59·85 | 61·05 | 63·09 | 64·63 |

These figures show quite clearly that the pentasulphide is formed and such a result would represent the gradual removal of the disulphide from a mixture of the two compounds. Nothing further can, however, be deduced from it, for the slow reaction $3(C_3H_7)_2S_4 \longrightarrow 2(C_3H_7)_2S_5 + (C_3H_7)_2S_2$ would require a curve of the same type.

That the formation of pentasulphides is not due to slow decomposition of the tetrasulphides was proved beyond doubt by an examination of the crude oil obtained by the action of sodium tetrasulphide on benzyl chloride. On extracting this oil with alcohol, dibenzyl disulphide was found to dissolve readily, whilst pure dibenzyl pentasulphide remained. It is concluded, therefore, that even if the tetrasulphide is first formed it changes practically instantaneously into a mixture of the di- and penta-sulphides.

## Experimental.

The sodium tetrasulphide and the alkali disulphides were prepared by Rule and Thomas's method (J., 1914, **105**, 177; see also Thomas and Jones, *loc. cit.*). The purity of the materials employed was established by analysis.

In every case except one, the reaction between the halogen compound (calculated quantity) and the metallic polysulphide was brought about in dry ether and in an atmosphere of hydrogen in the manner described in J., 1923, **123**, 3271. These reactions always took place slowly, but the speed varied considerably; in some cases reaction was complete in 3 or 4 days, in others in 2 months. The ether was then evaporated and the residual oil examined.

An experiment in which an aqueous solution of sodium disulphide was treated with allyl iodide gave an entirely different result; much decomposition took place and, instead of a disulphide, diallyl pentasulphide tetraiodide was obtained.

*Action of Sodium Tetrasulphide on some Organic Halogen Compounds.*

*Ethyl Iodide.*—Exactly the same procedure was followed as was employed in the case of potassium pentasulphide. Period of reaction 2 months. The clear, faintly yellow oil was kept over phosphoric oxide and paraffin wax for 5 days (Found: S = 58·4. Calc., for $Et_2S_5$, S = 68·82%). Under similar conditions, potassium pentasulphide yields practically pure diethyl pentasulphide.

The crude oil was then heated at 75° in a vacuum, until no further distillation occurred. A considerable quantity of ether first came over. This was observed in the case of every polysulphide examined, even although the material had been kept in a vacuum over phosphoric oxide and paraffin wax for several days. The existence of additive compounds of the organic polysulphides with ether thus appears to be indicated. A faintly yellow oil was then collected and this and also the residue were analysed [Found: S = 51·4 (distillate); S = 74·93 (residue). Calc. for $Et_2S_2$, S = 52·46; for $Et_2S_5$, S = 73·45%].

On one occasion, after the disulphide had been removed, a turbid, gelatinous residue was obtained which became clear and mobile when warmed. This proved to be a mixture of colloidal sulphur * with diethyl pentasulphide, the latter being identical with the

* This was the only example of the formation of colloidal sulphur met with by the authors amongst the many specimens of organic polysulphides examined. Mr. E. G. Jones, M.Sc., F.I.C., of the Liverpool City Laboratories informs us that similar observations have been made by him during the analysis of certain sulphur-containing drugs.

diethyl pentasulphide obtained from potassium pentasulphide (Found : S = 73·36. Calc. for $Et_2S_5$, S = 73·45%).

That this compound is certainly different from the tetrasulphide described by Chakravarti (J., 1923, **123**, 964) is proved by its behaviour when heated; sulphur is deposited, slowly at 70° and more rapidly as the temperature rises, distillation commences at about 155°, the temperature of the vapour remains constant for some time, and then rises to, but does not exceed, 185°. The distillate consists almost entirely of diethyl disulphide, b. p. 151°; the thick, reddish-brown residue is sulphur. The decomposition of diethyl pentasulphide thus follows the same course as that of the pentasulphides of the alkali metals. Chakravarti's compound boils at 210—212°, presumably under atmospheric pressure, without decomposition.

When estimating the sulphur in diethyl pentasulphide by the Carius method, nitric acid fumes were observed to attack the substance; fine, needle-shaped crystals of sulphur formed, and the liquid contained thioacetic and acetic acids and a small quantity of a sweet-smelling substance, believed to be acetal. The silver salts of the acids were isolated and identified.

*Propyl Bromide.*—Sodium tetrasulphide 5 gms.; period of reaction 8 weeks. The lemon-yellow oil was analysed [Found : S = 56·53. Calc. for $(C_3H_7)_2S_4$, S = 59·81; for $(C_3H_7)_2S_5$, S = 65·04%). A portion of the oil was heated in a vacuum at 80° for 4 days. A small quantity of liquid distilled, just sufficient to allow of a sulphur determination being made [Found : S = 43·5. Calc. for $(C_3H_7)_2S_2$, S = 42·66%]. The non-volatile residue, $d^{15°}$ 1·183, was dipropyl pentasulphide (Riding and Thomas, J., 1923, **123**, 3278) (Found : S = 64·74%).

*Allyl Iodide.*—Sodium tetrasulphide 5 gms.; period of reaction 4 days. The yield of the crude oil was very good but, in consequence of the formation of a considerable quantity of disulphide, the last traces of ether and of allyl iodide were difficult to remove [Found : S = 53·1. Calc. for $(C_3H_5)_2S_2$, S = 43·83; for $(C_3H_5)_2S_5$, S = 66·1%].

A portion of the oil was heated in a vacuum at 85° for several hours, a considerable quantity of distillate collecting. The products obtained were, however, very impure. A second portion of the original product was therefore heated in a vacuum over phosphoric oxide at a lower temperature, 65°, the object being to avoid decomposition as far as possible. The pump was kept going continuously. Similar products were obtained to those just described, but they were purer. It is thus advantageous to remove the disulphide at as low a temperature as possible [Found : S = 44·11 (distillate); S =

65·66 (non-volatile residue). Calc. for $(C_3H_5)_2S_2$, S = 43·83; for $(C_3H_5)_2S_5$, S = 66·1%]. The faintly yellow, highly refractive residue, $d^{18°}$ 1·249 (agreeing with that of the diallyl pentasulphide obtained by the action of allyl iodide on potassium pentasulphide), dissolved readily and completely in ether or pentane and no free sulphur could be detected. On treatment with iodine, diallyl pentasulphide tetraiodide (Thomas and Riding, this vol., p. 2216) was obtained (Found: I = 67·9. Calc., I = 67·7%).

*Benzyl Chloride.*—Sodium tetrasulphide 5 gms.; period of reaction 6 weeks. The light yellow oil was at once extracted with small quantities of dry alcohol (about 500 c.c. in all) to remove the disulphide and any remaining benzyl chloride, washed with ether, and, after this had evaporated, kept for 2 days over phosphoric oxide and paraffin wax in a vacuum desiccator (Found: C = 49·35; H = 4·00; S = 46·61. $C_{14}H_{14}S_5$ requires C = 49·13; H = 4·13; S = 46·75%).

The quantity of disulphide obtained, after purification, was insufficient for an analysis to be made. From the data given, however, there can be no doubt that the interaction of sodium tetrasulphide with halogenated organic compounds, under the conditions specified, results in the formation of a mixture of the penta- and di-sulphides of the radicals under examination.

### *Interaction between the Disulphides of the Alkali Metals and Halogenated Organic Compounds.*

*Ethyl Iodide.*—Sodium disulphide 5 gms.; period of reaction 2 months. The residual oil (yield 86%) was nearly pure diethyl disulphide (Found: S = 51·94. Calc., S = 52·46%). Yield after distillation (150—152°) 79%.

Several attempts were made to isolate the double compound with silver nitrate, $(C_2H_5)_2S_2,AgNO_3$, described by Price and Twiss (J., 1907, **91**, 2121), but it could never be obtained free from silver sulphide.

An attempt was made to prepare a compound,

$$(C_2H_5)_2S_2,C_3H_5I,HgI_2,$$

similar to those described by Rây (J., 1916, **109**, 131) by boiling a solution of allyl iodide and mercuric iodide in acetone with diethyl disulphide under reflux for 4 hours. The tarry product was purified by precipitating it several times from its acetone solution with much light petroleum. A strong solution in acetone of the black, apparently amorphous precipitate finally obtained was, after the addition of boiling water, boiled with animal charcoal for some hours, the liquid concentrated to 100 c.c., and the yellow crystals obtained (small yield) were recrystallised from acetone;

m. p. 94·6° (decomp.) [Found : I = 51·4; S = 5·4; Hg = 28·6. Calc. for $(C_2H_5)_2S_2,C_3H_5I,HgI_2$, I = 51·21; S = 8·6; Hg = 26·97%]. The low value for sulphur is in part explained by the fact that this determination is a long and tedious process. Rây (*loc. cit.*) has already pointed out that the results obtained are invariably much too low.

In order to show that mercuric iodide had not attached itself to allyl iodide at the double bond an experiment was made in which these two substances only were treated in the described manner. No evidence of combination could be found.

*Allyl Iodide.*—In one of the experiments with this substance, lithium disulphide, prepared by the method of Thomas and Jones (*loc. cit.*), was employed. The results were in no important respect different from those obtained with sodium disulphide, but the reaction was completed more quickly (5 days as against 3 weeks).

The oils remaining after evaporating the ether were distilled, the fraction, b. p. 76—82°/16 mm., being taken as pure diallyl disulphide. Yields varying between 66% and 75% were obtained, the lower yields being given by lithium disulphide. The following is a typical sulphur determination [Found : S = 42·97. Calc. for $(C_3H_5)_2S_2$, S = 43·82%]. The properties of the substance agreed with those of diallyl disulphide recorded by Semmler (*Arch. Pharm.*, 1892, **230**, 434), Bannerjee (J., 1911, **99**, 234; *Z. anorg. Chem.*, 1913, **83**, 113), Blanksma (*Rec. trav. chim.*, 1901, **20**, 121), Twiss (J., 1914, **105**, 39), and v. Braun (*Ber.*, 1903, **36**, 2265).

On treating the substance with an alcoholic solution of silver nitrate, yellow needles were obtained, believed to be $(C_3H_5)_2S_2,AgNO_3$. The substance, however, very rapidly decomposed, leaving a black residue of silver sulphide.

No precipitate formed on the addition of an alcoholic solution of mercuric chloride to the disulphide, but when the solution was diluted with water a heavy, white precipitate was immediately thrown down. This substance was dissolved in hot alcohol, reprecipitated by the slow addition of water, and dried (Found : S = 9·40; Hg = 61·77. Calc. for $C_6H_{12}O_2Cl_2S_2Hg_2$, S = 9·80; Hg = 61·59%). The constitution of this substance is at present uncertain. On keeping, it decomposes to some extent, mercurous chloride being formed.

*Action of Aqueous Solutions of Sodium Polysulphides on Allyl Iodide.*

To a solution of sodium hydrosulphide in water, sulphur was added in quantity sufficient completely to convert the hydrosulphide into disulphide. According to the view of Thomas and Rule (*loc. cit.*), such a solution would of course contain sodium tetrasulphide

and unchanged sodium hydrosulphide. To this solution, allyl iodide was then added in the amount theoretically required for the formation of diallyl disulphide, and the mixture was boiled under reflux. Considerable decomposition took place, acraldehyde and some unidentified acids being formed, together with a very viscous, heavy tar; very little disulphide was obtained. After drying, the tar yielded very little material to boiling alcohol, carbon disulphide, or ether, but chloroform resolved it into two portions, a thick syrup soluble in chloroform, and a reddish-brown solid. After several extractions, this solid was obtained as a micro-crystalline powder, m. p. 90°, similar in all its properties, except colour, to diallylpentasulphide tetraiodide (this vol., p. 2216) (Found: I = 67·50; S = 21·23. Calc. for $C_6H_{10}I_4S_5$, I = 67·70; S = 21·33%).

From the chloroform-soluble fraction, on addition of ether, a brown powder was precipitated. This was purified by reprecipitation several times (Found: S = 39·66; I = 23·5%). These figures appear to indicate a partly iodinated compound. The substance was therefore treated with iodine in the usual manner; the product was now diallyl pentasulphide tetraiodide.

The result of this experiment, coupled with the other work described in this paper, bears out the view that the action of sulphur on solutions of the hydrosulphides of the alkali metals yields one polysulphide only; in the case of sodium, the tetrasulphide.

*Summary.*

1. The action of halogenated organic compounds upon sodium tetrasulphide and also upon the disulphides of the alkali metals suspended in dry ether has been examined.

2. The disulphides of the alkali metals give rise to organic disulphides. From sodium tetrasulphide, however, a mixture of organic di- and penta-sulphides is obtained, the latter in much the greater quantity.

3. The bearing of these reactions on the question of polysulphide structure is briefly discussed and it is shown that it may be explained by the theory previously advanced by the authors concerning the structure of the inorganic polysulphides.

4. The oxidation of diethyl pentasulphide by nitrous fumes has been investigated and some new derivatives of the disulphides with alkyl halides and mercury halides have been prepared and examined.

5. The action of allyl iodide on aqueous solutions of sodium polysulphides, the sulphur being present in quantity sufficient for the formation of sodium disulphide, is shown to result in the formation of diallyl pentasulphide tetraiodide. This confirms the

view of Thomas and Rule regarding the nature of polysulphide solutions.

In conclusion, the authors desire to express their very sincere thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for much help and kindly criticism during the progress of this work.

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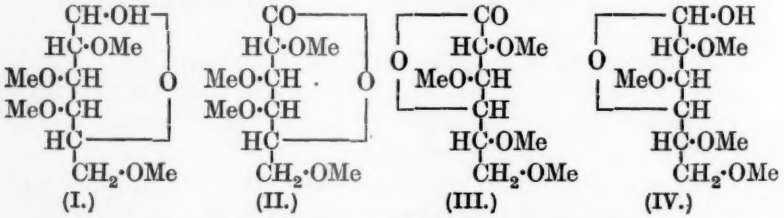
## CCCXXXVI.—*Amylene- and Butylene-oxidic Forms of Tetramethyl Galactose.*

By WALTER NORMAN HAWORTH, DAVID ARTHUR RUELL, and GEORGE CRONE WESTGARTH.

SOME confusion has entered into the literature relating to galactose and its methyl derivatives which it is important to dispel in view of the relation of this problem to the structure of lactose, melibiose, and raffinose. A recent paper by J. Pryde (J., 1923, **123**, 1808) has shown that the usual form of tetramethyl galactose probably has the amylene oxide structure (I), since oxidation of this substituted sugar leads to a δ-lactone (II) which is more dextrorotatory than the open-chain monobasic acid from which the lactone is derived and hence the oxide ring must be on the right (Hudson, *J. Amer. Chem. Soc.*, 1910, **32**, 338). On the other hand, a lactone having an opposite sign of rotation is obtained when galactonic acid is methylated, and the butylene oxide structure has been allocated to this form of tetramethyl galactonolactone (III) having the oxide ring on the left and conforming to a γ-lactone.




A scrutiny of the experimental evidence reported by Pryde reveals what seems at first a disconcerting fact, in that this author employed in the course of his work tetramethyl methylgalactoside, having $[\alpha]_D$ +4·4°, which was prepared by methylating galactose with methyl sulphate and sodium hydroxide. In view of the fact that both galactose and fructose show anomalous behaviour during

the ordinary process of glucoside formation with methyl-alcoholic hydrogen chloride at 100°, caution should be observed in attaching standard values to the methylated glucosides of these two hexoses prepared by any process of direct methylation. Galactose seems, indeed, to resemble fructose in its behaviour towards methyl sulphate and sodium hydroxide, and gives rise to a mixture of butylene-oxidic and amylene-oxidic forms (Haworth and Mitchell, unpublished result). The specific rotation quoted by Pryde for his specimen of tetramethyl methylgalactoside differs markedly from the standard value of either the α- or β-modification of this compound, which are respectively $[\alpha]_D$ +143·4° and +30·7° in water (Irvine and Cameron, J., 1904, **85**, 1076; 1905, **87**, 907), and the specimen probably contained structural isomerides. Moreover, the tetramethyl galactose derived from Pryde's specimen of galactoside showed the equilibrium value $[\alpha]_D$ +84·9° in water as compared with the standard value of +109°.

On repeating Pryde's oxidation of tetramethyl galactose and using an authentic specimen isolated from crystalline tetramethyl galactoseanilide, we found that the tetramethyl galactonolactone derived from it showed, in water, $[\alpha]_D$ +155° after 11 minutes, changing to +27·4° after 24 hours and was evidently the pure lactone (II). These values differ substantially from those quoted by the previous author, and leave no doubt that Pryde's specimen contained the isomeric form (III) as an impurity. The discrepancy does not, however, invalidate the reasoning or the conclusions of Pryde, since the impurity present in his specimen was fortunately insufficient to show a complete inversion of the sign of specific rotation.

When galactose is subjected to methylgalactoside formation in the cold, it gives rise to a pure form of *methylgalactoside* which has not previously been isolated. This form is strongly lævorotatory, and differs markedly from either of the known crystalline α- and β-forms isolated by Fischer, who conducted the glucoside formation at 100°. Complete methylation of this new compound leads to a *tetramethyl methylgalactoside* showing $[\alpha]_D$−45·2° in water, as compared with the figures for the normal α- and β-forms which are +143·4° and +30·7°. Hydrolysis gives rise to a tetramethyl galactose which reduces neutral permanganate, not, however, so rapidly as do γ-fructose derivatives. Its equilibrium value in water is $[\alpha]_D$−21·2° as contrasted with that of the normal tetramethyl galactose, which shows +109°. The behaviour of this new methylated galactose on oxidation indicates that it contains a 1 : 4-oxide, or butylene oxide structure on the reasoning of Hudson, since a tetramethyl galactonolactone was isolated having $[\alpha]_D$−27·1°,

changing only slightly in water to −25·2° by partial opening of the ring. These rotation values clearly show that the tetramethyl galactonolactone is identical with Pryde's second compound (III), isolated by methylation of the galactonolactone which was derived by the initial oxidation of the free unsubstituted sugar. Pryde's inference appears to us sound in ascribing to this the constitution of 2 : 3 : 5 : 6-tetramethyl galactonolactone, and consequently the structure we have allocated to the new form of methylated galactose is that of 2 : 3 : 5 : 6-tetramethyl galactose (IV). The galactoside corresponding to this sugar hydrolyses more easily than do the known pure forms of the normal α- and β-tetramethyl methylgalactosides, and, in this respect, as well as in the fact that the new sugar is unstable towards permanganate, it is to be regarded as having relationship with the γ-sugars.

Comparison of these results with those published by Miss Cunningham (J., 1918, **113**, 596) leads to the conclusion that the earlier claim to have isolated tetramethyl γ-methylgalactoside should be revised. The specific rotation of the supposed tetramethyl methylgalactoside is quoted as −4·3° or +8·8°, and a positive rotation is ascribed to the free sugar. The specimens appear to have been mixtures of both amylene- and butylene-oxidic forms, as may be inferred from the earlier work of Irvine and Cameron (*loc. cit.*) and from the fact that the original methylgalactoside formation was conducted at 100° in methyl-alcoholic hydrochloric acid. The observation that the mixture of methylated galactosides was completely hydrolysed during 8 hours by *N*/100-hydrochloric acid at 100° is in disagreement with the facts we have recorded, since *N*/50-acid requires a period of more than 40 hours for complete hydrolysis of the new (so-called γ-) form we have examined. The only deduction to be drawn is that the supposed tetramethyl γ-galactose of Miss Cunningham contained a large proportion of unhydrolysed galactosides after this treatment, and this view is substantiated by inspection of the recorded properties of the distillate, which seems to have been a first fraction. The analytical figures for this product agree on the whole more closely with those calculated for a tetramethyl methylgalactoside than for the formula of octamethyl digalactose which Miss Cunningham prefers. Moreover, the b. p. recorded (114—117°/0·03 mm.) is exactly in agreement with that of tetramethyl methylgalactoside, but is some 100° lower than would be expected for an octamethyl disaccharide. We are therefore of the opinion that the evidence for the "auto-condensation" of tetramethyl γ-galactose is inconclusive, and that the specimens of this sugar previously described were all mixtures of structural isomerides.

Since the amylene-oxidic form of tetramethyl galactose is isolated from the cleavage of methylated lactose, melibiose, and raffinose, it is established that the galactose residue occurring in the three latter sugars has the 1 : 5- or amylene-oxidic structure (compare Haworth and Leitch, J., 1918, **113**, 188; Haworth, Hirst, and Ruell, J., 1923, **123**, 3125).

## Experimental.

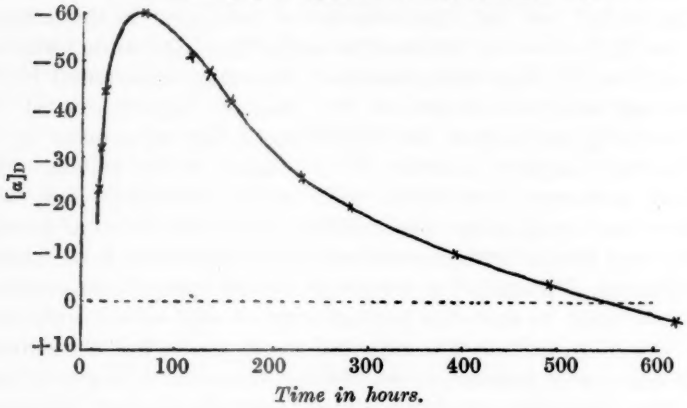
*Formation of* 1 : 4-*Oxidic Methylgalactoside.*—The experimental procedure described by E. Fischer (*Ber.*, 1914, **47**, 1985) for the preparation of γ-methylglucoside was imitated in that galactose was agitated with a 1% solution of hydrogen chloride in dry methyl alcohol at 15°, but the concentration of the sugar in this solution was varied between the limits of 0·5 and 5%. Glucoside formation was arrested in these experiments at the stage represented by the maximuml ævorotation and in the case of Experiment II this occurred 59½ hours from the beginning of the experiment or 17½ hours after complete solution of the sugar in the solvent. The mineral acid was neutralised with silver carbonate and, after filtration and evaporation, the residual syrup was dissolved in ethyl alcohol and treated with charcoal and, on evaporation, from 5 grams of galactose, 6 grams of a colourless, viscid syrup were obtained. In an attempt to test the homogeneity of this syrup, extraction with dry ethyl acetate was repeated many times, but the extracts yielded the same product as the residue, from which it was inferred that the substance consisted almost entirely of one individual. In all, four variations of the conditions of experiment were instituted, and the fact emerged that fineness of division of the sugar, efficient shaking in contact with the acid alcohol, and the concentration of the sugar solutions were the determining factors in effecting rapid solution of the sugar and rapid galactoside formation.

The curve in Fig. 1 illustrates the course of the reaction in experiment 1, using a 0·5% galactose solution, when the sugar dissolved after 6 hours, and after 49 hours was devoid of any action towards Fehling's solution. In this case a maximum lævorotation was attained, indicating the presence, very largely, of one stereochemical form of γ-methyl galactoside. With a 1·5% galactose solution, 42 hours were required for complete solution of the solid when the agitation was intermittent (Expt. II), but the maximum lævorotation was similarly $[\alpha]_D$ −58·1°. With a 4% mixture of the sugar, solution was attained in the acid-alcohol after 240 hours; but with 2% of galactose, solution was effected in only 27 hours by continuous and vigorous agitation.

*Methylation of the Methylgalactoside and Isolation of Tetramethyl Methylgalactoside.*—The syrupy methylgalactoside was methylated in the usual manner with methyl sulphate and sodium hydroxide (30% aqueous solution) and also with Purdie's reagents. On distillation of 10 g. of the product, 7·7 g. were collected as a colourless liquid, b. p. 112°/0·015 mm., showing $n_D$1·4405, $[\alpha]_D$—46·3° in ethyl alcohol and —45·2° in water ($c = 1·42$) [Found: C = 52·84; H = 8·47; OMe = 60·7. $C_6H_7O(OMe)_5$ requires C = 52·80; H = 8·80; OMe = 62·0%].

FIG. 1.

*Formation of γ-methylgalactoside (Experiment I).*




*Hydrolysis of 2 : 3 : 5 : 6-Tetramethyl Methylgalactoside.*—Digestion of the tetramethyl methylgalactoside with 0·137*N*-hydrochloric acid led to complete hydrolysis to the free sugar after 400 minutes at 95°. Polarimetric readings were taken during this procedure as follows:

| Time (mins.). | 0 | 20 | 30 | 45 | 60 | 120 | 210 |
|---|---|---|---|---|---|---|---|
| $[\alpha]_D$ | −44·2° | −49·2° | −50·4° | −50·3° | −47·8° | −36·5° | −24·7° |
| Time (mins.) | 285 | 405 | | | | | |
| $[\alpha]_D$ | −21·9° | −17·6° constant. | | | | | |

When this is represented by a graph, its form is identical with that shown by tetramethyl γ-methylglucoside on hydrolysis to the free sugar.

Hydrolysis was also effected by hydrochloric acid of greater dilution, and in one experiment using *N*/50-HCl, which is approximately one-seventh of the above concentration, the curve was of exactly the same form as above, but hydrolysis was slowed down to about one-seventh of the rate.

The product, 2 : 3 : 5 : 6-*tetramethyl galactose*, was isolated in the usual way, and was a colourless liquid, b. p. 136°/0·05 mm., having $n_D$ 1·4540; and $[\alpha]_D$ −21·2° in water ($c$ = 2·12) and this value was unchanged on keeping or catalysing the solution [Found: C = 50·62; H = 8·53; OMe = 51·6. $C_6H_8O_2(OMe)_4$ requires C = 50·84; H = 8·47; OMe = 52·5%].

*Oxidation: Isolation of* 2 : 3 : 5 : 6-*Tetramethyl Galactonolactone.*—The oxidation of the above specimen of tetramethyl galactose was conducted in aqueous solution by adding bromine water at 30—35° during 6½ hours. After keeping over-night, the solution was devoid of action towards Fehling's solution. The excess of bromine was removed by aeration and this was followed by treatment of the more concentrated solution with litharge and finally with silver oxide until neutral to litmus. The filtrate was saturated with hydrogen sulphide, again filtered, and the solution evaporated. Extraction with dry ether yielded a pale yellow syrup, which was twice distilled (b. p. 127—128°/0·02 mm.) and showed $n_D$ 1·4502; and $[\alpha]_D$ −27·1° in water ($c$ = 1·47), changing in 12 days to −25·2° (Found: C = 51·08; H = 7·79; OMe = 52·0. Calc., C = 51·28; H = 7·69; OMe = 53·0%. On titration, the compound behaved as a lactone and required, for 0·1473 g., 6·0 c.c. of $N$/10-NaOH; calc., 6·29 c.c.).

*Oxidation of* 2 : 3 : 4 : 6-*Tetramethyl Galactose: Isolation of* 2 : 3 : 4 : 6-*Tetramethyl Galactonic Acid and its Lactone.*—The tetramethyl galactose was obtained from the corresponding crystalline anilide by warming with 5% hydrochloric acid for some minutes. The pure distilled sugar prepared in this manner had the physical and chemical properties of authentic tetramethyl galactose of the normal type. The oxidation was conducted with bromine water as described above for the isomeric 2 : 3 : 5 : 6-tetramethyl galactose, and isolation of the product led to the recognition of two compounds, (*a*) a crystalline solid, sparingly soluble in ether, m. p. 84°, and (*b*) a syrup, b. p. 128°/0·03 mm., having $n_D$ 1·4571.

The crystals were identified by titration and analysis as 2 : 3 : 4 : 6-tetramethyl galactonic acid, showing $[\alpha]_D$ (initial) +22·6° in water ($c$ = 0·58), changing after 2 days to +26·6° (Found: C = 47·5; H = 8·04; OMe = 48·2. Calc., C = 47·62; H = 7·94; OMe = 49·2%. Titration: 0·0989 g. required 7·9 c.c. of $N$/20-NaOH; calc., 7·83 c.c.).

The syrup had the properties of a lactone and was also obtained by distilling the above crystalline tetramethyl galactonic acid under diminished pressure (Found: C = 50·9; H = 7·74; OMe = 52·7. Calc., C = 51·28; H = 7·69; OMe = 53·0%. 0·1558 g. of the tetramethyl galactonolactone required 6·5 c.c. of $N$/10-NaOH for neutralisation; calc., 6·6 c.c.).

Its specific rotation in water ($c = 1{\cdot}04$) was determined over a period of 24 hours.

| Time ..... | 11 mins. | 35 mins. | 2 hours | 24 hours |
|---|---|---|---|---|
| $[\alpha]_D$ ..... | +155·0° | +140·6° | 90·2° | 27·4° constant. |

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## CCCXXXVII.—*Aluminium Amalgam as a Reducing Agent in the Sugar Series.*

By DINSHAW RATTONJI NANJI and FREDERIC JAMES PATON.

SODIUM amalgam, first used by Bouchardat (*Ann. Chim. Phys.*, 1872, [iv], **27**, 74) for reducing a sugar (lactose), has the disadvantage that the alkali may cause the formation of abnormal products by isomeric change (Lobry de Bruyn and Van Eckenstein: Nef.). Scheibler (*Ber.*, 1883, **16**, 3010), discussing Krusemann's results (*ibid.*, 1876, **9**, 1465), who had obtained mannitol by the reduction of dextrose and lævulose, suggested that the dextrose was partly converted into lævulose, which then yielded mannitol. Fischer and Herz (*Ber.*, 1892, **3**, 539) recommended keeping the solution neutral by the addition from time to time of sulphuric acid; the sodium sulphate formed, however, increases the difficulty of isolating the reduction product. Neuberg and Marx (*Biochem. Z.*, 1907, **3**, 539) used calcium amalgam, which gives a neutral solution and insoluble calcium carbonate. Ipatiev (*Ber.*, 1912, **45**, 3218) and Senderens (*Compt. rend.*, 1920, **170**, 45) employed a direct hydrogenation method with nickel and nickel oxide as catalyst, whilst Cake (*J. Amer. Chem. Soc.*, 1922, **44**, 859) hydrogenised in alkaline solution with platinum-black as catalyst.

Wislicenus and Kaufmann (*Ber.*, 1895, **45**, 1323) introduced aluminium amalgam as a reducing agent. We find that, in neutral solutions, this reagent is almost without action on the sugars, but when a trace of ammonia is present mannose and galactose may be reduced to the extent of 80—95%, whilst the alcohols may be isolated in a yield of 55% of the sugar employed. We find it advantageous to employ four equivalents of the amalgam, and we believe the beneficial effects of ammonia to be due to the formation from the aldose used of compounds of the aldehyde-ammonia type

(Ling and Nanji, *J. Soc. Chem. Ind.*, 1923, **41**, 151T). The reduction of maltose and lactose is less satisfactory, apparently owing to hydrolysis by the active hydrogen.

## Experimental.

The following exploratory experiments were carried out with glucose.

Table A.

| Temp. | Conc. of glucose %. | Solvent. | Amt. of Al. (multiple of theor. quant.). | % Reduction. |
|---|---|---|---|---|
| 15° | 10 | 82% Alcohol. | 2 | Negligible. |
| ,, | ,, | ,, | 4 | ,, |
| ,, | ,, | 48% ,, | 2 | ,, |
| ,, | ,, | ,, | 4 | 5 |
| ,, | ,, | Water. | ,, | 15 |
| ,, | 20 | Water + 1 c.c. ammonia. | 2 | 28 |
| 45–50° | 25 | Water + 0·75 c.c. ammonia. | ,, | 48 |
| ,, | ,, | ,, ,, ,, | 4 | 86 |
| ,, | 20 | 50% Alcohol + 1 c.c. amm. | ,, | 49 |
| ,, | 25 | Water + 0·5 c.c. ammonia. | ,, | 90 |
| ,, | ,, | ,, ,, ,, | 6 | 92 |
| ,, | ,, | Water + 5 c.c. ammonia. | ,, | 90–92 |

The extent of reduction was determined approximately by titration with Fehling's solution in presence of the aluminium hydroxide dissolved in an excess of alkali. Filtration of the aluminium hydroxide was avoided on account of its high adsorptive power.

*Reduction of Glucose.*—Aluminium (10 g.) in small turnings is covered with water, which is then heated to boiling, a little caustic soda is added, and, as soon as hydrogen comes off vigorously, the liquid is decanted, and the aluminium washed free from alkali with cold water by decantation. The cleaned aluminium is left for 5 minutes under 0·5% mercuric chloride, washed by decantation, 100 c.c. of 25% glucose solution and 1 c.c. of ammonia (*d* 0·880) are added, the temperature during the reaction is kept at 45—55°, and after some hours the sorbitol is isolated. Since the alumina cannot be filtered off readily even after passing carbon dioxide, it is precipitated in alcoholic solution by sulphuric or by oxalic acid. In the former case, alcohol is added until the concentration is 60% and then one-third of the amount of sulphuric acid necessary to produce the normal sulphate. After boiling for 30 minutes and cooling in ice, the solution can be filtered by suction from the aluminium sulphate, which may be extracted again with 60% alcohol containing a little acid. The alcohol is distilled from the filtrate, and after concentration the last traces of aluminium and sulphuric acid are removed by boiling with excess of barium carbonate.

Oxalic acid is used in the same way, except that the alcohol is made up to 40% and the final traces are removed by calcium carbonate. To remove unchanged glucose, the solution is fermented with yeast after boiling with norit, which adsorbs the colloidal mercury and decolorises the solution. When the solution no longer reduces Fehling's solution, it is evaporated to dryness, the residue extracted with 80% alcohol, and the sorbitol precipitated in a crystalline form by adding absolute alcohol. The anhydrous sorbitol must be quickly filtered, washed, and placed in a vacuum desiccator. Yield 60%.

*Reduction of Mannose.*—This is carried out in a manner similar to the above, except that one-third of the mannitol can be obtained at once after passing carbon dioxide, which here renders the alumina capable of filtration. The remainder is obtained from the alumina by extracting twice by the oxalic acid method. Fermentation may be avoided, for mannitol crystallises more readily than sorbitol and can be freed from mannose by one or two crystallisations from dilute alcohol. Yield 55—58%.

*Reduction of Galactose.*—Carbon dioxide is passed, as with mannose. Dulcitol, being slightly soluble in water, crystallises readily, but separation from galactose is best achieved by crystallisation from 30—40% alcohol, washing with 80% alcohol and finally with a little 40% alcohol. Yield 55—60%.

Our thanks are due to Dr. R. Seligman for a supply of aluminium.

DEPARTMENT OF THE BIOCHEMISTRY OF FERMENTATION,
UNIVERSITY OF BIRMINGHAM. [*Received, September 23rd,* 1924.]

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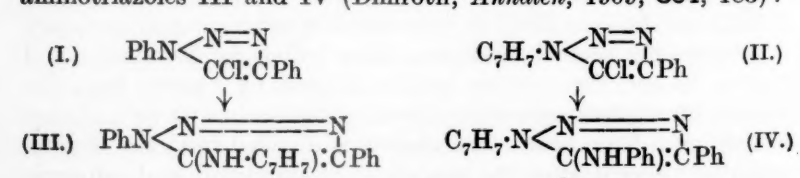
# CCCXXXVIII.—2 : 5-*Iminodihydro*-1 : 2 : 3-*triazole*. *Part II.*

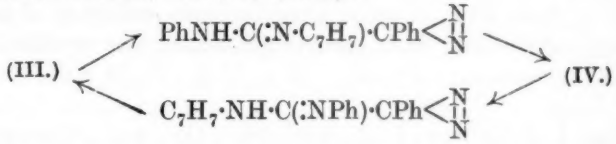
By HELEN WINIFRED CARNELLEY and PAVITRA KUMAR DUTT.

THE reactions between 5-chloro-1 : 4-diphenyl-1 : 2 : 3-triazole (I) (Dimroth, *Annalen*, 1904, **335**, 102) and *p*-toluidine on the one hand and between 5-chloro-4-phenyl-1-*p*-tolyl-1 : 2 : 3-triazole (II) and aniline on the other would be expected to yield the isomeric aminotriazoles III and IV (Dimroth, *Annalen*, 1909, **364**, 183):




Actually a mixture of the same two compounds A (m. p. 227—

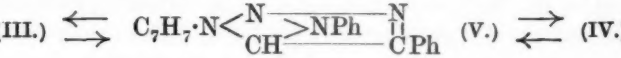
228°) and B (m. p. 171—172°), having the expected composition $C_{21}H_{18}N_4$, is obtained in each case. Since both A and B can be converted into an equilibrium mixture by the action of heat, they are tautomeric. Assuming that they have the formulæ III and IV, this change could be represented by the following scheme (Dimroth, *Annalen*, 1910, **373**, 345):




It is difficult to accept this explanation as correct, because substances of the types III and IV undergo isomeric change without evolution of nitrogen when treated with boiling alcoholic sodium ethoxide, whereas diazoacetic ester under the same treatment is easily converted into glycollic ester with evolution of nitrogen.

The compounds A and B cannot be acetylated by boiling with acetic anhydride and sodium acetate, only an equilibrium mixture of the two being formed. Acetylation, however, takes place on prolonged boiling with acetic anhydride and acetyl chloride.

Nitrous acid has no action on A and B in suspension in hydrochloric acid; in solution in glacial acetic acid, the compound A yields apparently an additive product which does not give Liebermann's test, and B yields a mononitro-compound; both give nitrosoamines in alcoholic hydrochloric acid. The difference in behaviour in the second case suggests that A and B are structurally different; the mechanism of the change may be represented by the following scheme (compare Part I, J., 1923, **123**, 265):




By the action of boiling alcoholic hydrochloric acid on A and also by the hydrolysis of its nitroso-derivative, an equilibrium mixture of isomerides was obtained from which the substance A has been isolated; the other isomeride, B, was apparently not formed. This isomeric change thus appears to be different from what is produced by the action of heat. Further work is in progress to elucidate this point and also to determine the constitutions of A and B.

## EXPERIMENTAL.

5-Hydroxy-1 : 4-diphenyl-1 : 2 : 3-triazole was prepared essentially by the method of Dimroth (*loc. cit.*); the triazole was regenerated from the isolated sodium salt, instead of from the total liquid, by acidification. It was thus obtained in a purer state, although

in slightly inferior yield (60 g. from 70 g. of ethyl phenylacetate and 48 g. of phenylazoimide). It melted at 160° and after crystallisation from alcohol formed fine needles, m. p. 166° (decomp.), whereas Dimroth records for the substance an indefinite form and the melting point 150—151° (Found: N = 17·8; calc., 17·7%).

5-*Hydroxy*-4-*phenyl*-1-p-*tolyl*-1 : 2 : 3-*triazole*, prepared similarly (yield 55 g. from 70 g. of ethyl phenylacetate and 50 g. of *p*-tolylazoimide), crystallised from methyl alcohol in fine needles, m. p. 173—174° (decomp.) (Found: N = 17·0. $C_{15}H_{13}ON_3$ requires N = 16·7 %).

5-Chloro-1 : 4-diphenyl-1 : 2 : 3-triazole (I) was obtained in improved yield by modifying Dimroth's method as follows. To 30 g. of phosphorus pentachloride in 250 c.c. of benzene at 70—80°, 30 g. of 5-hydroxy-1 : 4-diphenyl-1 : 2 : 3-triazole were added gradually, and the mixture was heated under reflux until the evolution of hydrochloric acid had ceased. After removing benzene and phosphoryl chloride under reduced pressure, and crystallising the residue from methyl alcohol, 15—16 g. of the chloro-compound (I) were obtained, m. p. 137—138° (Found: Cl = 13·6; calc., 13·9 %). Dimroth gives m. p. 137°.

5-*Chloro*-4-*phenyl*-1-p-*tolyl*-1 : 2 : 3-*triazole* (II), prepared similarly (yield 14—15 g. from 30 g. of the corresponding hydroxy-triazole), crystallised from methyl alcohol in colourless needles, m. p. 124—125° (Found: N = 15·7; Cl = 13·1. $C_{15}H_{12}N_3Cl$ requires N = 15·6; Cl = 13·2 %).

*Action of* p-*Toluidine on Substance I.*—Condensation of the substances I and II with *p*-toluidine and aniline, respectively, does not take place so readily as in the case of the chloro-compounds described in the first paper (*loc. cit.*). The following method, however, worked equally satisfactorily for both. The chloro-compound I (7 g.), 15 g. of *p*-toluidine, and 20 c.c. of absolute alcohol were heated together in a sealed tube at 110—120° for about 16 hours and then at 135—145° for 6—8 hours. After steam-distillation, the solid residue was filtered, and crystallised from absolute alcohol; the yield of crude A, m. p. 223—225°, was usually 5—6 g. Recrystallised several times from the same solvent with the aid of animal charcoal, it was obtained in colourless, shining, rhombic plates, m. p. 227—228° (Found: C = 77·6; H = 5·7; N = 17·2. $C_{21}H_{18}N_4$ requires C = 77·3; H = 5·5; N = 17·2 %).

The solubility of the compound A in cold absolute alcohol is about 0·5 %, and 15 % in the solvent previously saturated with hydrogen chloride. It is sparingly soluble in methyl alcohol, benzene, acetic anhydride, or cold glacial acetic acid and insoluble in water, ligroin, or cold concentrated hydrochloric acid. In boiling concentrated

hydrochloric acid, it dissolves to the extent of 0·1 g. per litre without suffering decomposition.

The alcoholic mother-liquor from the first crystallisation of A, on evaporation, gave, in addition to a little more of A, another substance (B) which, on being recrystallised several times from absolute alcohol with the aid of animal charcoal, was obtained in colourless needles having a woolly texture (yield about 0·5 g.); m. p. 171—172° after shrinkage at 169° (Found : C = 77·6; H = 5·7; N = 17·3 %). The purity of the two products A and B was also tested under the microscope, when only one form of crystals was observed in each case. In addition to the rhombic plates and needles, a few hexagonal plates were observed in both A and impure fractions of B. Measurement of the angles proved them to be of the same system as the rhombic plates.

The substance B is slightly more soluble than A in the solvents named above, except in hydrochloric acid.

*Action of Aniline on Substance II.*—From 7 g. of the chloro-compound II, 20 c.c. of aniline, and 20 c.c. of absolute alcohol, treated exactly as in the preceding case, the same two products (A and B) were obtained, as shown by mixed melting points and crystalline forms, and in very much the same proportion.

*Action of Heat on* A *and* B.—Two grams of each substance were heated separately with 20 c.c. of absolute alcohol in sealed tubes at 135—145° for 24 hours. There was apparently no decomposition, as no increase of pressure was noticed when the tubes were opened. By repeated crystallisation from absolute alcohol, about 1·3 g. of A and 0·2 g. of B (identified by mixed melting points) could be recovered from each tube.

*Action of Nitrous Acid on* A *and* B.—(*a*) In acetic acid solution : I. To a cooled solution of A (2 g.) in 300 c.c. of glacial acetic acid, 2 g. of sodium nitrite were added gradually during 2 hours. The mixture was left for 24 hours, when it gave no reaction for nitrous acid. The bright yellow, crystalline precipitate obtained on dilution of the liquid with a large bulk of water was collected, washed with water, and dried (yield 2·2 g.). With Liebermann's reagent, the crude product gave a light green solution, due to the presence of a trace of the nitrosoamine. On carefully recrystallising the crude product from a cold mixture of glacial acetic acid and methyl alcohol by evaporation in a vacuum desiccator, a small quantity of light yellow needles was obtained which gave a yellow solution with Liebermann's reagent. The purified product melted indefinitely with decomposition at 135—140° and its analysis indicated the addition product $C_{21}H_{18}N_4,HNO_2$ (Found : C = 67·9; H = 4·9; N = 18·1. Calc., C = 67·6; H = 5·1; N = 18·8 %).

The crude product decomposed when its alcoholic solution was boiled and yielded another substance, crystallising in dull yellow prisms, m. p. 196—198° (without decomp.). With Liebermann's reagent, it gave a yellow solution. It has not yet been obtained in the pure state (Found: C = 70·28, 71·59; H = 4·77, 5·02; N = 16·54, 16·91 %).

In order to find whether the yellow substance mentioned above (m. p. 135—140°) is a product of nitration, a solution of 2 g. of A in 300 c.c. of glacial acetic acid was treated in the cold with 1 c.c. of fuming nitric acid. After 24 hours, the solution was diluted with water, the yellow precipitate collected (2·4 g.), and recrystallised from methyl alcohol and glacial acetic acid; yellow needles, m. p. 193—194° (without decomp.) (Found: N = 20·25. Calc. for dinitro-compound, N = 20·19 %). The stability of this product in boiling solvents and also at its melting point shows that the two derivatives must be constitutionally different.

II. The substance B (1 g. in 100 c.c. of glacial acetic acid) was treated in the cold with sodium nitrite (1 g.) as in the case of A. The crude product (1 g.) gave a much fainter green colour with Liebermann's reagent. On recrystallisation from benzene–methyl alcohol (hot or cold), it separated in long, flat, yellow needles, m. p. 197—198° (without decomp.) (Found: C = 68·3; H = 4·5; N = 19·1. Calc. for the mononitro-derivative, C = 67·9; H = 4·6; N = 18·8 %). With Liebermann's reagent, it gave an orange solution.

(*b*) In alcoholic hydrochloric acid solution.—The substance A (2 g.) was dissolved in the cold in 25 c.c. of absolute alcohol, previously saturated with hydrogen chloride, and diluted with 100 c.c. of rectified spirit. Sodium nitrite (1 g. in 5 c.c. of water) was slowly added. After 12 hours, the yellow mixture was diluted with one litre of water, the dull yellow precipitate collected (2·1 g.), and recrystallised from methyl alcohol (hot or cold); various impure fractions were obtained which decomposed at about 140° and gave the nitrosoamine reaction.

In another experiment, the whole of the crude nitrosoamine was hydrolysed by warming on the water-bath with aqueous alcoholic hydrochloric acid for ½ hour. The pink solid obtained on dilution was collected (1·9 g.). It melted indefinitely at 210—217° and gave more than a trace of nitrosoamine when treated with sodium nitrite in acetic acid solution. Its analysis agrees with that of the original substance A (Found: C = 76·5; H = 5·7; N = 17·3 % in the crude product).

Exactly the same product was obtained by boiling an alcoholic solution of A in a current of hydrogen chloride for 8—10 hours.

On recrystallisation, the pure substance A was isolated, and various impure fractions which crystallised in colourless, lenticular crystals, m. p. 215—219° (Found : C = 77·6; H = 5·7; N = 17·3 %). The product is evidently an equilibrated mixture of isomerides.

The isomeride B, when treated with nitrous acid in alcoholic hydrochloric acid, yielded a mixture of yellow and colourless needles which gave the characteristic nitrosoamine reaction. Owing to the difficulty of preparing this isomeride in quantity, it has not been possible to study the hydrolysis of its nitroso-derivative.

*Acetylation of* A *and* B.—I. Two grams of the substance A were boiled under reflux for 24 hours with a mixture of 30 c.c. of acetic anhydride and 30 c.c. of acetyl chloride. The reaction took place very slowly with evolution of hydrogen chloride and finally a clear solution was obtained. The solid product (2·1 g.) that separated on pouring this into water was collected and crystallised from methyl alcohol. After several crystallisations, 0·5 g. of colourless, rhombic prisms were obtained, m. p. 114—115° (Found : C = 74·6; H = 5·6; N = 15·3. $C_{23}H_{20}ON_4$ requires C = 75·0; H = 5·4; N = 15·2 %).

The acetyl derivative is extremely soluble in the ordinary organic solvents. On prolonged boiling with alcoholic hydrochloric acid, it was hydrolysed, giving the same equilibrium mixture (m. p. 210—217°) as was obtained by the action of alcoholic hydrochloric acid on A.

II. The substance B was acetylated in the same way as above. The crude product after one crystallisation from methyl alcohol gave the pure acetyl derivative, monoclinic prisms, m. p. 126—127° (Found : C = 74·7; H = 5·7; N = 15·3 %). This is also easily soluble in the common organic solvents.

In conclusion, we desire to thank Professor J. B. Cohen, F.R.S., for helpful criticism, and the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

THE UNIVERSITY, LEEDS. [*Received, April 10th,* 1924.]

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## CCCXXXIX.—*Behaviour of Nitrophenols with* p-*Toluenesulphonyl Chloride.*

By SHRIRANG M. SANÉ and SHIAM SUNDER JOSHI.

ULLMANN and his collaborators have shown (*Ber.*, 1908, **41**, 1870, 3939; 1911, **44**, 3731) that nitrophenols react with *p*-toluenesulphonyl chloride in two ways : mononitrophenols form *p*-toluene-

sulphonyl esters in presence of sodium carbonate or diethylaniline: polynitrophenols, with sodium carbonate as condensing agent, also yield such esters, but in presence of diethylaniline are converted into polynitrochlorobenzenes.

The behaviour of the following nitrophenols, and also of 2 : 4 : 6-tribromophenol towards *p*-toluenesulphonyl chloride has now been investigated; 6-chloro-2 : 4-dinitro-*m*-cresol alone behaved abnormally, in that in presence of diethylaniline it was converted into the *p*-toluenesulphonyl ester.

2 : 4 : 6-*Tribromophenyl* p-*Toluenesulphonate*. — A mixture of 2 : 4 : 6-tribromophenol (6·5 gms.), *p*-toluenesulphonyl chloride (4·5 gms.), and diethylaniline (14 gms.) was heated on the water-bath for 4 hours, cooled, and digested with dilute hydrochloric acid; the brown liquid, which solidified on rubbing, separated from alcohol in colourless crystals, m. p. 113° (yield 5 gms.). 0·3989 gave 0·1884 $BaSO_4$; S = 6·5. $C_{13}H_9O_3Br_3S$ requires S = 6·6%.

4 : 6-*Dibromo*-2-*nitrophenyl* p-*toluenesulphonate* was obtained from a mixture of 4 : 6-dibromo-2-nitrophenol (6 gms.), *p*-toluenesulphonyl chloride (4·5 gms.), and diethylaniline (14 gms.); colourless crystals from alcohol, m. p. 140° (yield 5 gms.). 0·3276 gave 0·1662 $BaSO_4$; S = 6·97. $C_{13}H_9O_5NBr_2S$ requires S = 7·11%.

2 : 6-*Dibromo*-4-*nitrophenyl* p-*toluenesulphonate* was obtained from 2 : 6-dibromo-4-nitrophenol, *p*-toluenesulphonyl chloride, and diethylaniline; colourless crystals from alcohol; m. p. 128—129°. 0·3900 gave 0·1998 $BaSO_4$; S = 7·02. $C_{13}H_9O_5NBr_2S$ requires S = 7·11%.

2-*Bromo*-4 : 6-*dinitrophenyl* p-*toluenesulphonate*, colourless crystals from alcohol, m. p. 157° (yield 5 gms.), was obtained by gradually adding sodium carbonate (2·5 gms.) to a suspension of 2-bromo-4 : 6-dinitrophenol (6 gms.) and *p*-toluenesulphonyl chloride (5 gms.) in boiling water. 0·3656 gave 0·2043 $BaSO_4$; S = 7·7. $C_{13}H_9O_7N_2BrS$ requires S = 7·7%.

1-*Chloro*-2-*bromo*-4 : 6-*dinitrobenzene*. — A mixture of 2-bromo-4 : 6-dinitrophenol (12 gms.), *p*-toluenesulphonyl chloride (10 gms.), and diethylaniline (24 gms.) was heated on the water-bath for 4 hours, cooled, and digested with dilute hydrochloric acid; the brown liquid solidified on rubbing (yield 10 gms.); colourless crystals from alcohol, m. p. 63°. 0·2584 gave 24·4 c.c. of N (28°, 729 mm.); N = 10·27. 0·2070 gave 0·2416 AgCl + AgBr; Cl + Br = 40·67. $C_6H_2O_4N_2ClBr$ requires N = 9·96; Cl + Br = 41%.

The lability of the chlorine atom in this compound was shown by the following experiments. 2-Bromo-4 : 6-dinitroaniline, yellow crystals from benzene, m. p. 153° (Found: N = 15·97. Calc., N = 16·04%), was obtained (yield 2 gms.) by passing dry ammonia

for 45 minutes into a boiling alcoholic solution of 1-chloro-2-bromo-4 : 6-dinitrobenzene (2·6 gms.). *2-Bromo-4 : 6-dinitrodiphenylamine*, orange-yellow crystals from benzene, m. p. 150°, was obtained (yield 2·5 gms.) when a mixture of 1-chloro-2-bromo-4 : 6-dinitrobenzene (2·8 gms.), aniline (1 c.c.), sodium acetate (5 gms.), and sufficient alcohol was heated on the water-bath for one hour, cooled, and filtered. 0·2080 gave 22·6 c.c. of N (20°, 741 mm.); N = 12·35. 0·3694 gave 0·2071 AgBr; Br = 23·85. $C_{12}H_8O_4N_3Br$ requires N = 12·43; Br = 23·65%. 2 : 4-Dinitrophenoxazine, reddish-violet, silky needles, m. p. 215°, from acetic acid, was obtained in a similar way from 1-chloro-2-bromo-4 : 6-dinitrobenzene (2 gms.), *o*-aminophenol (1·2 gms.), sodium acetate (5·5 gms.), and alcohol (yield 1·8 gms.) (Found: N = 14·95; C = 52·74; H = 2·86. Calc., N = 15·39; C = 52·73; H = 2·58%). *2-Bromo-4 : 6-dinitrodimethylaniline*, orange-red crystals from alcohol, m. p. 96°, was obtained when 1-chloro-2-bromo-4 : 6-dinitrobenzene (1·5 gms.) was heated with dimethylaniline and sufficient alcohol on the water-bath for 1 hour (yield 1·3 gms.). 0·2322 gave 32 c.c of N (38°, 725 mm.); N = 14·43. $C_8H_8O_4N_3Br$ requires N = 14·48%. *Dibromotetranitrodiphenyl*-p-*phenylenediamine*, purple-red crystals, m. p. above 340°, separated when a mixture of 1-chloro-2-bromo-4 : 6-dinitrobenzene (2·8 gms.), *p*-phenylenediamine (0·6 gm.), sodium acetate (6 gms.), and sufficient alcohol was heated on the water-bath for 1 hour and cooled (yield 2·7 gms.). 0·3616 gave 47·1 c.c. of N (38°, 727 mm.); N = 13·68. $C_{18}H_{10}O_3N_6Br_2$ requires N = 14·05%.

*6-Chloro-2 : 4-dinitro*-m-*tolyl* p-*toluenesulphonate* was obtained from a mixture of 6-chloro-2 : 4-dinitro-*m*-cresol (2·3 gms.; prepared from 6-chloro-*m*-cresol and nitric acid, *d* 1·5, in acetic acid; compare Walther and Zipper, *J. pr. Chem.*, 1915, [ii], **91**, 413), *p*-toluenesulphonyl chloride (2 gms.), and diethylaniline (5 gms.); colourless crystals from benzene, m. p. 125° (yield 3 gms.). 0·5660 gave 0·3310 $BaSO_4$; S = 8·03. $C_{14}H_{11}O_7N_2ClS$ requires S = 8·3%.

*3-Chlorodinitrophenol.*—*m*-Chlorophenol (6·5 gms.) was added gradually to a cooled mixture (20 c.c.) of equal parts of fuming nitric acid and acetic acid, the mixture then warmed on the water-bath, and the nitro-compound precipitated by addition of water (yield 4 gms.); colourless crystals from alcohol, m. p. 92°. 0·2646 gave 29·4 c.c. N (20°, 744 mm.); N = 12·7. $C_6H_3O_5N_2Cl$ requires N = 12·8%.

A trinitro-compound remained in the solution.

*1 : 3-Dichlorodinitrobenzene.*—A mixture of the preceding 3-chlorodinitrophenol (4·5 gms.; presumably 3-chloro-4 : 6-dinitrophenol, m. p. 92° [compare Fries and Roth, *Annalen*, 1912, **389**, 344]),

*p*-toluenesulphonyl chloride (4 gms.), and diethylaniline (8 gms.) was heated on the water-bath for 4 hours, cooled, and digested with dilute hydrochloric acid; the brown liquid which separated solidified on cooling; colourless crystals from acetic acid, m. p. 102° (yield 4 gms.). 0·2030 gave 0·2430 AgCl; Cl = 29·6. $C_6H_2O_4N_2Cl_2$ requires Cl = 29·9%.

1 : 3-Dichloro-4 : 6-dinitrobenzene has m. p. 102° (Nietzki and Schedler, *Ber.*, 1897, **30**, 1666), but we are not yet prepared to assert the identity of the two compounds.

THE UNIVERSITY, LUCKNOW. [*Received, May 5th*, 1924.]

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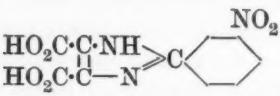
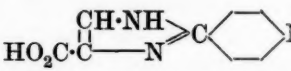
## CCCXL.—*Substitution in the Benzene Nucleus on Nitration of 2-Phenylglyoxaline and its Carboxylic Acids.*

By FRANK LEE PYMAN and EDMUND STANLEY.

MONONITRATION of 4-phenylglyoxaline gave 4-*p*- and 4-*o*-nitrophenylglyoxalines in yields amounting to 69 and 25% of the theoretical (Grant and Pyman, J., 1921, **119**, 1893). Application of the same method to 2-phenylglyoxaline gave a smaller total yield of nitrophenylglyoxalines, for part of the nitric acid was used up in oxidising some of the initial material to benzoic acid, but here again the *p*-isomeride predominated, 2-p-, 2-o-, and 2-m-*nitrophenylglyoxalines* being isolated in yields amounting to 50, 1·5, and 0·2% of the theoretical, respectively. In view of this result, the nitration product of 2-phenylglyoxaline-4 : 5-dicarboxylic acid, assumed by Fargher (J., 1921, **119**, 163) to be the *m*-isomeride, has been re-examined and found to be a mixture of 2-m-*nitrophenylglyoxaline*-4 : 5-*dicarboxylic acid* (I) with the *p*-isomeride, since it gave, on decarboxylation, 52% of *m*- and 19% of *p*-2-nitrophenylglyoxaline. The *m*-dicarboxylic acid was isolated in a pure state.

(I.) 

 (II.)

The effect of a single carboxyl group was then tested by the nitration of 2-phenylglyoxaline-4(or 5)-carboxylic acid, when the product, from which 2-p-*nitrophenylglyoxaline*-4(*or* 5)-*carboxylic acid* (II) can be isolated, gave, on decarboxylation, 52% of *p*- and 19% of *m*-2-nitrophenylglyoxaline.

The introduction of carboxyl groups into the glyoxaline nucleus of 2-phenylglyoxaline thus progressively diminishes the ratio of

para- to meta-nitration of the benzene nucleus. The results of nitration seem to us to be associated with the fact that 2-phenylglyoxaline and its monocarboxylic acid yield salts with mineral acids, whereas 2-phenylglyoxaline-4 : 5-dicarboxylic acid does not. On this basis, the results may be partly systematised on the assumption that the key to the orientating influence is the character of the doubly-linked nitrogen atom, by reference either to its state of saturation after Flürscheim, or to its polarity after Lapworth. Employing the second method, the predominant meta-substitution in the case of the dicarboxylic acid may be ascribed to the negative polarity of the doubly-linked nitrogen atom, and the predominant para (and ortho)-formation in the case of 2-phenylglyoxaline and its monocarboxylic acid to the fact that, in these compounds, the nitrogen is rendered, more or less, positive by salt formation. The difference of orientating properties would thus resemble that between $\cdot NH_2$ and $\cdot NH_3X$. Fargher's view (*loc. cit.*) that the meta-nitration of 2-phenylglyoxaline-4 : 5-dicarboxylic acid is due to the predominating negative character of the glyoxaline dicarboxylic acid substituent is seen to be unsatisfactory on considering the results of nitration of phenylacetic acid.

## Experimental.

*Nitration of 2-Phenylglyoxaline.*—Anhydrous 2-phenylglyoxaline nitrate (12 g.) was added to 24 c.c. of sulphuric acid below 30°, and the solution heated for ½ hour in boiling water. After basifying with sodium carbonate, the hot solution (about 300 c.c.) was filtered from the crude *p*-isomeride and kept, when further material was deposited. Crystallisation of these crops as nitrate gave respectively 2-*p*-nitrophenylglyoxaline nitrate (50% of theory) and 2-*m*-nitrophenylglyoxaline nitrate (0·2% of theory). The original mother-liquor on acidification and extraction with ether gave 0·6 g. of crude benzoic acid. All mother-liquors were then basified and extracted with ether, when, on concentration, crude 2-*o*-nitrophenylglyoxaline separated and was purified by crystallisation from water (1·5% of theory). The ethereal mother-liquor contained crude 2-phenylglyoxaline, which was identified as picrate.

2-p-*Nitrophenylglyoxaline* crystallises from alcohol in small, yellow needles, m. p. 310—315° (decomp.; corr.). It is sparingly soluble in hot alcohol and insoluble in hot water, ether, or chloroform [0·1435 gave 0·3001 $CO_2$ and 0·0476 $H_2O$. C = 57·5; H = 3·7. 0·1098 gave 21·2 c.c. $N_2$ (22°, 765 mm.). N = 22·3. $C_9H_7O_2N_3$ requires C = 57·1; H = 3·7; N = 22·2%]. The *nitrate* crystallises from water in yellowish-brown prisms containing $2H_2O$ which are gradually lost on exposure to the air. (Loss at 100° : on material air-

dried for 4 hours, = 12·6; on material air-dried for 3 weeks, = 0·9. $C_9H_7O_2N_3,HNO_3,2H_2O$ requires $H_2O = 12·5\%$). The dried salt melts and decomposes at 172° (corr.) [0·1364 gave 0·2137 $CO_2$ and 0·0408 $H_2O$. C = 42·7; H = 3·4. 0·1105 gave 21·6 c.c. $N_2$ (16°, 745 mm.). N = 22·6. $C_9H_7O_2N_3,HNO_3$ requires C = 42·8; H = 3·2; N = 22·2%]. The *picrate* crystallises from hot alcohol, in which it is sparingly soluble, in fine, yellow needles, m. p. 262° (corr.) [0·1393 gave 0·2188 $CO_2$ and 0·0295 $H_2O$. C = 42·8; H = 2·4. 0·1674 gave 28·9 c.c. $N_2$ (17°, 755 mm.). N = 20·2. $C_9H_7O_2N_3,C_6H_3O_7N_3$ requires C = 43·1; H = 2·4; N = 20·1%].

2-m-*Nitrophenylglyoxaline* crystallises from hot water or alcohol in fine, very pale yellow needles, m. p. 193—194° (corr.). It is sparingly soluble in hot water, readily soluble in hot alcohol, but almost insoluble in ether or chloroform [0·1426 gave 0·2974 $CO_2$ and 0·0487 $H_2O$. C = 56·9; H = 3·8. 0·1470 gave 28·2 c.c. $N_2$ (15°, 754 mm.). N = 22·6%].* The *nitrate* crystallises from water in long, straw-coloured plates, m. p. 182° (decomp.; corr.) [0·1798 gave 0·2813 $CO_2$ and 0·0524 $H_2O$. C = 42·6; H = 3·3. 0·1034 gave 20·0 c.c. $N_2$ (19°, 761 mm.). N = 22·6%].* The *picrate* crystallises from water in long, silky, yellow needles, m. p. 245—246° (corr.) [0·1002 gave 17·0 c.c. $N_2$ (14°, 749 mm.). N = 19·9%].*

2-o-*Nitrophenylglyoxaline* crystallises from water in large, nearly colourless plates, m. p. 188—189° (corr.). It is sparingly soluble in hot water, readily soluble in alcohol, slightly soluble in chloroform, and almost insoluble in ether [0·1618 gave 0·3383 $CO_2$ and 0·0546 $H_2O$. C = 57·0; H = 3·8. 0·1338 gave 24·7 c.c. $N_2$ (15°, 762 mm.). N = 21·9%].* The *nitrate* crystallises from water in nearly colourless prisms, m. p. 153—154° (corr.). The *picrate* crystallises from water in long, silky, yellow needles, m. p. 212° (corr.).

The three isomeric 2-nitrophenylglyoxalines are insoluble in aqueous ammonia or sodium carbonate, but dissolve in aqueous sodium hydroxide, yielding yellow to orange-red solutions, the intensity of the colour being in the order $p>o>m$.

The constitutions of the three isomerides were determined by the method employed by Grant and Pyman (J., 1921, **119**, 1893) in the case of the nitro-derivatives of 4-phenylglyoxaline, namely, oxidation with permanganate and identification of the corresponding nitrobenzoic acids.

*Nitration of 2-Phenylglyoxaline-4-carboxylic Acid.*—Nine grams of *2-phenylglyoxaline-4-carboxylic acid nitrate* [wedge-shaped plates from dilute nitric acid, m. p. 188° (decomp.; corr.). Found: N = 16·9. $C_{10}H_8O_2N_2,HNO_3$ requires N = 16·7%] were added to 18 c.c. of cooled strong sulphuric acid, and the solution was heated for one

* The calculated values have been given above for the *p*-isomeride.

hour in boiling water, diluted with water (100 c.c.), and kept. The sulphates crystallised out, whilst the mother-liquor gave the bases on adding a limited quantity of sodium hydroxide. The products were crystallised fractionally as sulphates from 5*N*-sulphuric acid, and the bases liberated from the pure salts by treatment with water.

2-p-*Nitrophenylglyoxaline-4-carboxylic acid* (yield 3·0 g.) forms bright yellow needles, very sparingly soluble in water, melts and effervesces at 288° (corr.), then resolidifies and melts again at 308° (0·1203 gave 0·2268 $CO_2$ and 0·0360 $H_2O$. C = 51·4; H = 3·4. $C_{10}H_7O_4N_3$ requires C = 51·5; H = 3·0%). On heating with water at 200°, it yields 2-*p*-nitrophenylglyoxaline. The *sulphate* separates from 5*N*-sulphuric acid in nearly colourless prisms, m. p. 286° (decomp.; corr.), containing about $2H_2O$ [Found: loss at 100° = 7·0; calc., 6·0%. 0·2493, dried at 100°, gave 0·1022 $BaSO_4$. S = 5·6. $(C_{10}H_7O_4N_3)_2,H_2SO_4$ requires S = 5·7%].

2-m-*Nitrophenylglyoxaline-4-carboxylic acid* (yield 0·2 g.) forms colourless needles, very sparingly soluble in water, and melts and effervesces at 248° (corr.), yielding pure 2-*m*-nitrophenylglyoxaline. The *sulphate* separates from 5*N*-sulphuric acid in long, straw-coloured plates, decomp. 230°.

*Decarboxylation of the Nitration Product of 2-Phenylglyoxaline-4-carboxylic Acid.*—A solution of 2-phenylglyoxaline-4-carboxylic acid nitrate (8·0 g.) in 16 c.c. of concentrated sulphuric acid was heated for 1 hour in boiling water, poured into water, and mixed with sufficient sodium hydroxide to leave it just acid to methyl-orange, when the mixed nitro-derivatives separated (yield 6·0 g., *i.e.*, 81%). Two grams of this product were heated with 20 c.c. of water for 6 hours at 240°, and the resulting nitrophenylglyoxalines were separated as described above, when 52% of 2-*p*- and 18% of 2-*m*-nitrophenylglyoxalines were isolated in a pure state.

The identity of the products was established by mixed melting point determinations of the base and nitrate in each case.

*Nitration of 2-Phenylglyoxaline-4 : 5-dicarboxylic Acid.*—The crude precipitated acid (A) prepared by Fargher's method (*loc. cit.*) [yield 77%; m. p. with effervescence 266° (corr.)] was converted into the ammonium salt, which was crystallised several times from water, when it formed silky needles, m. p. 297—298° (corr.). On acidifying an aqueous solution of the salt, the acid was precipitated and after crystallisation from water formed long, straw-coloured needles, m. p. 279° (corr.). It was identified as 2-m-*nitrophenylglyoxaline-4 : 5-dicarboxylic acid* by heating with 10 parts of water for 6 hours at 200°, when 2-*m*-nitrophenylglyoxaline unaccompanied by the *p*-isomeride was obtained.

*Decarboxylation of the Crude Nitration Product.*—9·25 Grams of A were heated in a bath at 270—280° until effervescence ceased, and the residue (6·25 g.) was crystallised fractionally as nitrate or base, when 52% of *m*- and 19% of *p*-2-nitrophenylglyoxaline were isolated in a pure state. The identity of the products was established by mixed melting point determinations of the base and nitrate in each case. A similar result was obtained when the decarboxylation was carried out by heating the acid with water at 200°.

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## CCCXLI.—*Extraction of the Isomeric Xylenes from Crude Xylol.*

By T. S. PATTERSON, ANDREW MCMILLAN, and ROBERT SOMERVILLE.

DURING the war we worked out a method of separating *m*-xylene from coal-tar, and coke-oven, xylene, and from Borneo petroleum, a problem regarding which little appears in the literature, although it proved to be a very simple one. Our ultimate procedure was as follows: * A sample (2400 c.c.) of coke-oven xylene (b. p. 137—141°) was shaken on a machine in four bottles with 3600 c.c. of ordinary concentrated sulphuric acid (*d* 1·84) for about ¾ hour. The mixture became slightly warm—up to about 40°—and the time of shaking depended a little on the temperature developed. The residue amounted to 141 c.c., from which a stronger sulphuric acid absorbed 135 c.c. presumably of *p*-xylene; the remainder, we suppose, was petroleum. To the acid liquid, 2560 c.c. of water were slowly added with stirring. On standing over-night or by cooling to about 10°, the mass went almost solid. After vigorous shaking, the resulting pasty crystals were removed by filtration; yield of moist crystals = 5376 g.

Of this crude sulphonic acid, 1500 g. were heated in a 2-litre distilling flask on an oil-bath. At 130° (thermometer in acid), steam at 150—200° was blown through the liquid, and during the earlier part of the distillation 1 part of condensed steam brought over about 4 parts of *m*-xylene. In all, 472 c.c. of *m*-xylene were brought over in 1¼ hours by about 500 c.c. of condensed steam. Taking this as the true yield, the whole 5376 g. of sulphonic acid should produce 1691 c.c. of *m*-xylene, which, calculated on the

* Clarke and Taylor (*J. Amer. Chem. Soc.*, **1923**, **45**, 831) have recently published some work on the subject. Our results, whilst not overlapping, supplement and amplify theirs.

2259 g. originally absorbed by the sulphuric acid, is equivalent to 74·9%. The product was of a slightly better quality, as will be explained below, than a sample of Merck's pure *m*-xylene (pre-war). By crystallising the sulphonic acid as described below, the quality of the xylene could easily be improved.

The acid obtained is doubtless a mixture of *o*- and *m*-xylenesulphonic acids. It is very soluble in water and in alcohol, but can easily be recrystallised by melting it and then adding about one-third of its bulk of 33% sulphuric acid. This would probably be the simplest procedure on a large scale. To obtain a pure specimen of the acid, which does not appear hitherto to have been described, it is best to recrystallise the crude product from chloroform, adherent water being removed by running the warm solution through filter-paper. After three crystallisations, it melted at 61—62°, and yielded a sulphonyl chloride which, with ammonia, gave a sulphonamide melting at 136—137° (Jacobsen, *Ber.*, 1878, **11**, 18). This identifies the acid as *m*-xylene-4-sulphonic acid, the sodium salt of which has already been obtained by Clarke and Taylor (*loc. cit.*).

The melting point of some *m*-xylene, prepared from a sample of acid which had been crystallised three times from chloroform, was determined by means of a pentane thermometer and liquid air. The uncorrected results along with those for other products were as follows :

Crude coke-oven xylene — 70°, Merck's pure *m*-xylene — 47°, xylene from sulphonic acid (not recrystallised) — 45·5°, *m*-xylene from sulphonic acid crystallised thrice from chloroform — 40·5°. By applying the proper correction to the last reading, a value close to — 53°, which is stated to be the m. p. of pure synthetic *m*-xylene, was obtained.

*Calcium* m-*xylene*-4-*sulphonate* forms light, flaky crystals. It is easily soluble in water at the ordinary temperature, but becomes much less soluble as the temperature rises. From the concentrated solution it therefore separates on heating.

o-*Xylene*-4-*sulphonic acid* was made, for purposes of comparison with the preceding acid, by the method described above, using a sample of Kahlbaum's *o*-xylene. From the sulphuric acid solution, the *o*-xylenesulphonic acid separates in the same manner as the *m*-xylenesulphonic acid, and it also can be crystallised from chloroform, but is much more difficult to obtain pure on account of its hygroscopic character. Long standing on a porous plate in a vacuum desiccator gave a product, m. p. 63—64°. It was converted into the chloride, and this into the sulphonamide, m. p. 143—144° (Jacobsen, *Ber.*, 1878, **11**, 22).

*Calcium o-xylene-4-sulphonate*, unlike the salt derived from *m*-xylene, is a fine, granular solid, soluble in hot water, but much less soluble in cold water than is the *m*-xylene derivative. It is thus differentiated markedly from the *m*-xylene derivative, and a simple method of separating the two acids is accordingly available. This method we applied to the separation of *o*-xylene from the crude coke-oven xylol referred to above. From 625 c.c. of the crude product there were obtained, by distillation with an ordinary rod and disc fractionating column, 45 c.c. of a fraction, b. p. 139—142°. This was converted into the corresponding calcium sulphonates. On concentrating the solution, a white, flaky mass of calcium *m*-xylenesulphonate separated at the boiling point, and was filtered off. This was repeated until all the calcium *m*-xylenesulphonate appeared to be removed. The filtrate was then cooled in ice and calcium *o*-xylenesulphonate crystallised out. The weight of the salt so obtained was 50 g., corresponding to a yield of 4·7% of *o*-xylene on the original sample.

The properties of these salts afford a simple test for determining roughly the purity of *o*-xylene. From a sample of *o*-xylene obtained from The British Drug Houses, Ltd., the calcium sulphonate was prepared. On concentrating the solution, a white solid separated at the boiling point, which redissolved on cooling the solution, thus showing the presence of an appreciable amount of *m*-xylene in the specimen.

These results suggest an interesting lecture experiment. By mixing together 2·5 g. of calcium *o*-xylenesulphonate, 0·5 g. of calcium *m*-xylenesulphonate, and 8 c.c. of water, a mixture is obtained which is liquid at 50°, and on cooling in ice-water goes almost solid owing to the separation of calcium *o*-xylenesulphonate, whereas on heating at 100° it again goes almost solid, but this time owing to the separation of calcium *m*-xylenesulphonate. Starting from a low temperature, the semi-solid mass passes gradually into solution, which is complete at 50°, and then, on heating to a higher temperature, the mixture goes almost solid again.

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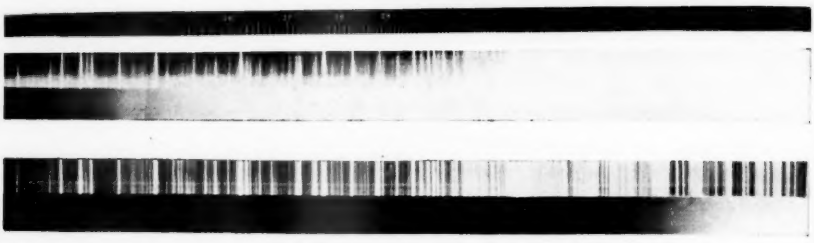
PLATE I



[*To face Trans., p.* 2491 ]

# CCCXLII.—*A Spectroscopic Study of the Luminescent Oxidation of Phosphorus.*

By Harry Julius Emeléus and William Eric Downey.

The slow oxidation of phosphorus is such a unique and, in some respects, anomalous process that it is strange to find a close parallel to one of its peculiarities in the common burning of the element. The direct study of this peculiarity, the luminescence, has received scant attention, for the literature contains only two accounts of spectroscopic investigations of the glow.

Centnerszwer and Petrikaln (*Z. physikal. Chem.*, 1912, **80**, 235) were the first to show that the light from glowing phosphorus gives more than a continuous spectrum in the visible region. It gives some bands, which may be regarded as characteristic, in the ultra-violet region. These investigators found fourteen "lines" between $\lambda = 2381$ Å.U. and $\lambda = 2613$ Å.U. and a band at $\lambda = 3252$ Å.U. More recently, Petrikaln (*Z. Physik*, 1924, **22**, 119) has repeated the work with a somewhat different result. Instead of the narrow bands or "lines" formerly obtained, he now finds four bands, which he is unable to resolve into smaller bands. These broad bands occur in positions which would cover the narrow bands previously obtained.

The work described below was undertaken to find whether burning phosphorus emits light of which the spectrum is similar to that of the glow. If the oxidation process which causes the glow were the same as that taking place when the element burns vigorously, it might be expected that the two light-emissions would give similar spectra. Experiment has now shown that phosphorus burning under various conditions always emits light which has fundamentally the same spectrum. The differences observed are that the bands become broader and the light intensity in the visible region becomes greater with increase in temperature of the light source. This is to be expected, for the higher the temperature of a substance the greater the thermal agitation of the molecules and hence, a broadening of the bands. Also, a higher temperature entails an increase in black-body radiation, that is, light purely due to the temperature of a body.

The spectrum of the flame of phosphorus burning in air under reduced pressure is closely similar to that of the glow obtained by Centnerszwer and Petrikaln, but shows no trace of the broad bands described by Petrikaln as occurring in the glow spectrum. Petrikaln's glow spectrum resembles rather that of phosphorus burning in enriched air. As he mentions that the phosphorus sometimes

melted and caught fire, his experiment was repeated and an exposure obtained in which the possibility of a flame had been eliminated. The result bears out the earlier work, and it is suggested that Petrikaln did not obtain the narrow bands because the occasional fires caused them to be masked by the broad bands.

## EXPERIMENTAL.

The whole of the spectrograms were taken on a Hilger small quartz spectrograph. The linear dispersion between $\lambda = 2294$ Å.U. and $\lambda = 2618$ Å.U. is 14 mm. The focal lengths of the lenses are 203 mm. A diaphragm was used in front of the slit to enable comparison spectra to be taken. A copper arc was used for comparison purposes. The wave-lengths of the copper arc lines have been accurately measured by Hasbach (*Z. wiss. Phot.*, 1914, **13**, 399).

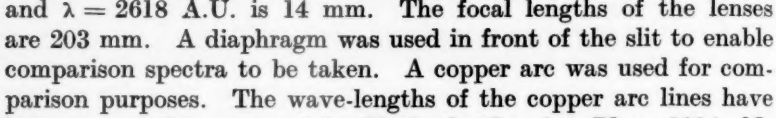



Fig. 1

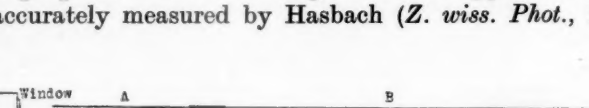



Fig. 2

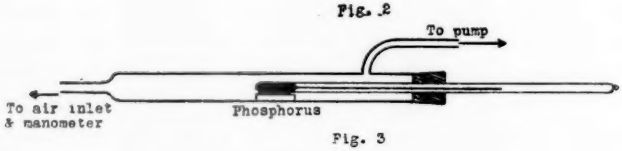



Fig. 3

*The Spectrum of the Flame of Phosphorus burning in Enriched Air.*

In this experiment the apparatus shown in Fig. 1 was used. A piece of well-annealed hard glass tubing (A), 30 cm. long and 1·5 cm. in diameter, was connected to a length of soft glass tubing (B), 100 cm. long. The latter tube was connected to a water-pump and contained a lightly packed plug of glass wool, as shown, to stop the solid products of combustion. These tubes were capable of a transverse motion along the line of the axis of the collimator. The slit of the spectrograph was protected by a quartz window 2 mm. thick. The method of experiment was as follows. A short length of thin stick phosphorus was ignited in A in a slow stream of air, enriched by oxygen, which was being drawn through the tubes by the pump. The gas passing over the phosphorus

contained about 80% of oxygen. When the phosphorus, after about 3 minutes, had burned away, the tubes were drawn back, a fresh piece of phosphorus was put in, and the procedure repeated. Owing to the intense heat, A occasionally broke and had to be renewed. After the necessary exposure, the diaphragm in front of the slit was moved and an exposure to the copper arc made.

The temperature of the flame was measured by means of a platinum–platinum 10% rhodium thermocouple. The junction was enclosed in a thin silica tube, which was placed in the flame. The highest recorded temperature was 800°.

The exposures to the phosphorus flame were varied from a few seconds to 12 hours. The first photograph (Plate I) is an enlargement from a plate exposed for 8 hours. It shows bands at $\lambda =$ 2390 Å.U., $\lambda = 2475$ Å.U., and $\lambda = 2530$ Å.U., whilst the original plate shows another at $\lambda = 2630$ Å.U. The continuous background masks the latter band and completely conceals the band shown in the second photograph. This is taken from a plate exposed for about 20 seconds. Here, the bands of shorter wavelength are missing, but a complex band appears between $\lambda = 3245$ Å.U. and 3275 Å.U.

*The Spectrum of the Flame of Phosphorus burning in Air under Reduced Pressure.*

The apparatus shown in Fig. 2 was used for obtaining the combustion of phosphorus in air under reduced pressure. A soft glass tube, 30 cm. by 1·2 cm., had a quartz window, 2 mm. thick, sealed on to one end. A side tube, as shown, made connexion with a manometer and an adjustable air inlet. A piece of dry phosphorus was put in the tube about 5 cm. from the window and a plug of glass wool near the other end of the tube, which was connected to a water-pump. The pressure in the tube was reduced and the air inlet adjusted to maintain the air pressure at about 5 cm. of mercury. In this way, air passed over the phosphorus at the rate of 20 c.c. per minute. The air inlet being adjusted, the phosphorus was warmed just to the ignition point and then burned with a steady yellowish-green flame for about an hour. Duplicate apparatus enabled a change to be made in a few minutes.

To measure the temperature of the flame, the apparatus described above was modified (Fig. 3). The phosphorus being burnt under the same conditions as when it was being used for a light source, the average temperature of the flame was 125°.

The third photograph is reproduced from a plate which was exposed for 60 hours. The bright continuous spectrum which was so strongly developed in the hot flame has almost vanished. The

members of the broad bands are separated and appear more as lines. The band at $\lambda = 3245$—$3275$ Å.U. reveals a very complicated structure, which is better shown in the fifth photograph. This was taken from the same plate.

The lines were measured in the usual manner, using the Cornu-Hartmann formula connecting wave-lengths in a prism-spectrum. The smallness of the dispersion of the instrument does not warrant the wave-lengths being given more accurately than to the nearest unit.

TABLE I.

| λ. | ν. | λ. | ν. |
|---|---|---|---|
| 3418 | | 2633 | 37,980 |
| 3413 | | 2619 | 38,180 |
| 3408 | | 2607 | 38,360 |
| 3390 | | 2594 | 38,530 |
| 3383 | | | |
| 3311 | | 2552 | 39,180 |
| 3302 | | 2537 | 39,410 |
| 3296 | | 2527 | 39,580 |
| 3290 | | | |
| 3285 | | 2477 | 40,380 |
| | | 2475 | 40,400 |
| 3278 | 30,500 | 2463 | 40,600 |
| 3273 | 30,550 | 2462 | 40,620 |
| 3268 | 30,590 | 2451 | 40,800 |
| 3265 | 30,630 | | |
| | | 2393 | 41,790 |
| 3254 | 30,740 | 2385 | 41,930 |
| 3249 | 30,780 | 2380 | 42,020 |
| 3245 | 30,820 | 2371 | 42,180 |

Although the bands of shorter wave-length appear almost as narrow as lines, in the case of the ones at $\lambda = 2475$ Å.U. and $\lambda = 2462$ Å.U. there are signs of further resolution. In each of these two bands a faint satellite on the longer wave-length side can be discerned in the original plate.

Attempts to detect regularities in the wave numbers have not met with success. A long exposure on an instrument of large dispersion would be necessary if any such regularities are to be sought.

*The Spectrum of the Light from Glowing Phosphorus.*

In this experiment the source consisted of a slab of phosphorus, 3 cm. × 4 cm. × 0·3 cm., cast in a shallow tin tray which was held vertically in front of the slit. Three nozzles served to conduct away the fumes and ensure a current of fresh air over the surface of the phosphorus. A stream of water playing on the back of the tray effectively prevented the phosphorus from catching fire. The surface of the phosphorus was washed morning and evening and the slab was renewed after 4 days. Continuing in this way, an exposure

of over 200 hours was made. After exposure to a copper arc, the plate was sensitised by Wood's method (*Astrophys. J.*, 1908, **27**, 379).

The fourth photograph is reproduced from the plate obtained in the above manner. The visible part of the spectrum is less intense than in the low-temperature flame. The narrow bands are weak but quite definite. There is no trace of broad bands superimposed on these narrow bands.

*Summary.*

This paper describes the spectroscopic examination of the light emitted when phosphorus burns. It is shown that:

1. When phosphorus burns in enriched air with a flame temperature of 800°, it shows five bands in the ultra-violet portion of the spectrum. These occur at $\lambda = 2390$, 2475, 2530, 2630, and 3275 Å.U.

2. When phosphorus burns in air under reduced pressure with a flame temperature of 125°, it emits the same bands as mentioned in (1), but they are resolved into smaller bands.

3. When phosphorus glows, it emits the same narrow bands as the low-temperature flame does. This contradicts Petrikaln's recent work, but agrees with the earlier work of Centnerszwer and Petrikaln.

We wish to thank Professor H. B. Baker, F.R.S., in whose laboratory the work has been done, for his kind interest at all times. We are also indebted to Professor A. Fowler, F.R.S., for much valuable advice during the progress of the work. The completion of the research was rendered possible by the award to one of us (H.J.E.) of a maintenance grant for which he desires to thank the Advisory Council of the Department of Scientific and Industrial Research, and to the other of us (W.E.D.) of a fellowship for which he thanks the Trustees of the Beit Fellowships for Scientific Research.

[*Received, October* 21*st*, 1924.]

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## CCCXLIII.—*Studies in Electro-endosmosis. Part II.*

By Fred Fairbrother.

Experimental evidence is now put forward in support of the view (Fairbrother and Mastin, this vol., p. 2319) that the calculation of the potential gradient, in electro-endosmosis experiments, from the observed current flow and the resistance of the electrolyte is

inadvisable, since the amount of current flowing through a fine capillary tube filled with a dilute solution of an electrolyte would be influenced by surface effects.

The idea that as a consequence of electro-endosmosis a liquid would show a greater conductivity in the capillary pores of a powder diaphragm than in bulk form was first put forward by Smoluchowski (*Anzeiger Akad. Wiss. Krakau*, 1903, *A*, 182) on theoretical grounds, and was confirmed experimentally by Stock (*ibid.*, 1912, *A*, 635) in the case of several organic liquids in quartz powder. Smoluchowski considered that in " good conducting salt solutions " the additional or surface conductivity would be quite negligible. McBain and Darke (*Trans. Faraday Soc.*, 1920, **16**, 150) state that the conductivity of a solution of potassium chloride in a quartz capillary tube of $\frac{1}{4}$ mm. bore is several units per cent. higher than its conductivity measured in bulk in the open.

The present experiments refer to diaphragms of powdered material.

## Experimental.

After several materials had been tested, the following determinations were carried out with carborundum powder and powdered Jena " Geräte " glass. The latter had been sieved so that it passed an 80-mesh sieve and was retained by a 120-mesh; the grains were of various shapes and had an average diameter of 0·2 to 0·25 mm. The carborundum powder was 100-mesh, was more uniform than the glass powder, and the grains had an average diameter of about 0·2 mm. Both were carefully purified before use and transferred to the cells under water. Powdered crystalline alumina (alundum) and quartz powder, in the form of crushed crystalline quartz and quartzite, are too liable to chemical attack on the surface to give trustworthy results. The carborundum and Jena glass were quite free from this defect, the resistances being fairly constant over many hours.

One of the most serious difficulties encountered was the reproducibility of the " piling " or packing of the powder. Stock states (*loc. cit.*) that quartz sand settles down after a time. The error thus introduced in his experiments, however, is relatively much smaller than that in the present case, because the increased conductivity which he measured was generally much greater.

The difficulty was overcome as far as possible in the following way. The powder, which had been rinsed in the cell twelve times with the solution, was packed as closely as possible by tapping the conductivity cell. Very little subsequent settling took place. After the resistance had been determined, the powder was shaken up in the cell full of solution, tapped into position again, and left

for a short time in the thermostat; the resistance was then redetermined. This was repeated a number of times, usually twenty. The average deviation of the individual readings from the mean of the series was generally less than 1% in the case of the carborundum and from 1 to 2% in the case of the glass. The less degree of accuracy in the latter case is to be attributed to the less uniform nature of the powder.

The conductivity cells which held the powders, a separate one being used for each, were made of Jena $16^{III}$ (normal) glass. The platinum electrodes, about 2·25 sq. cm. in area, were 0·5 mm. thick and were very rigid. They were separated by about 5 mm. and rigidly held relative to one another by glass bridges at the corners, sealed to the platinum. A third conductivity cell, C, was filled with the electrolyte in use, and the resistance determined at the beginning and the end of a series.

The resistances were measured by an alternating-current Wheatstone bridge with a six-dial resistance box ($10^5$—$10^{-1}\omega$) and slide-wire settings very near the middle, a current of about 1000 cycles per second, produced by a thermionic valve, being used. The valve generator was housed in a box lined with sheet iron. In the case of the more concentrated solutions and in all the carborundum experiments (*vide infra*), the polarisation was compensated by a variable condenser in parallel with the resistance box. An electrically heated thermostat was used at a temperature of $20° \pm 0{\cdot}01°$.

In the following tables, $R_C$ is the resistance of cell C filled with the solution alone, $R'_A$ is the mean resistance of cell A containing the powdered glass and solution, and $R'_B$ is the resistance of cell B containing carborundum and solution, all in ohms. The powder in each case filled about $\frac{1}{2}$ to $\frac{2}{3}$ of the cell, extending further above the electrodes than the distance of the latter apart. The same amount of powder was used throughout. The concentrations of solutions given are approximate. The solution of aluminium chloride was made from the commercial salt and allowed to stand until the aluminium hydroxide had settled out.

In the case of a diaphragm of powdered material the dimensions of the canals between the grains and hence the theoretical resistance of the circuit cannot be calculated unless the grains are approximately spherical and uniform. It becomes necessary for the sake of comparison to assume that in a particular case the surface conductivity is negligible and that the resistance of the cell is made up of the resistance of the electrolyte and the mechanical hindrance offered by the powder. In the present work, the ratios $R'_A/R_C$ for $N/100$-solutions of the three acids, hydrochloric, sulphuric, and sulphosalicylic acid, in the glass powder are greater than in

TABLE I.

*Jena Glass.*

| Electrolyte. | Conc. | $R_C$. | $R'_A$. | $R'_A/R_C$. | $(\lambda+\delta\lambda)/\lambda$. |
|---|---|---|---|---|---|
| KCl ..... | $N/10{,}000$ | 13,515 | 56,250 | 4·16 | 1·17 |
| „ ..... | $N/1{,}000$ | 1,507 | 6,998 | 4·66 | 1·05 |
| „ ..... | $N/100$ | 158·4 | 743·4 | 4·69 | 1·04 |
| „ ..... | $N/10$ | 17·35 | 80·5 | 4·64 | 1·05 |
| HCl ..... | $N/10{,}000$ | 5,100 | 23,730 | 4·65 | 1·05 |
| „ ..... | $N/1{,}000$ | 519·4 | 2,478 | 4·77 | 1·02 |
| „ ..... | $N/100$ | 52·8 | 254·7 | 4·82 | 1·01 |
| Sulphosalicylic acid ... | $N/100$ | 93·0 | 449·5 | 4·83 | 1·01 |
| $H_2SO_4$ ..... | $N/100$ | 62·6 | 304·7 | 4·87 | 1·00 |
| Acetic acid ..... | $N/1{,}000$ | 4,448 | 20,080 | 4·51 | 1·08 |
| „ ..... | $N/100$ | 1,354 | 6,274 | 4·62 | 1·05 |
| „ ..... | $N/10$ | 414·8 | 1,966 | 4·74 | 1·03 |
| $AlCl_3$ ..... | $M/1{,}000$ | 701·0 | 3,164 | 4·51 | 1·08 |
| „ ..... | $M/100$ | 84·8 | 389·1 | 4·59 | 1·06 |

any other case, and within the limits of the experiment are equal. It seems logical to assume, therefore, that here the surface conductivity is negligible, an assumption which is supported by the known behaviour of these acids in decreasing electro-endosmosis.

Stronger solutions of acids were not employed for fear of introducing resistance errors in consequence of polarisation.

In the right hand column of Table I are given the relative increases in apparent conductivity on this basis. These are obtained as follows.

The resistance of, say, cell A, containing only an electrolyte of conductivity $\lambda$, is $R_A = l/q\lambda$, where $l/q$ is a factor depending on the area and disposition of the electrodes. If the space between the electrodes be now filled with a powder, $R'_A = l'/q'\lambda$ (neglecting surface conductivity), $l'/q'$ depending, not only on the electrodes, but also on the size and arrangement of the canals in the powder. If surface conductivity also is present, then $R'_A = l'/q'(\lambda + \delta\lambda)$, and therefore

$$\frac{R'_A}{R_A} = \frac{l'q}{lq'} \cdot \frac{\lambda}{\lambda + \delta\lambda}.$$

If we assume that $\lambda/(\lambda + \delta\lambda)$ is unity in the case of $N/100$-sulphuric acid, we can get a measure of $l'q/lq'$, and, in the case of another electrolyte X,

$$\frac{R'_{A(H_2SO_4)}}{R_A} \Big/ \frac{R'_{A(X)}}{R_A} = \frac{\lambda+\delta\lambda}{\lambda}.$$

Instead of measuring $R_A$ in the same cell, A, it is more convenient to measure the resistance of an auxiliary cell C, filled with the electrolyte; otherwise it becomes necessary to empty out the powder even between determinations with successive concentrations

of the same electrolyte. Since we are dealing with a ratio, $R_C$ can be substituted for $R_A$, assuming a constant ratio of the "cell constants" over the range of electrolytes examined.

It may be seen from Table I that dilute electrolytes exhibit an additional conductivity in the capillaries of glass powder. The values of $\delta\lambda$ are in most cases greater than the estimated experimental error.

As might have been expected, the surface conductivity increases in dilute solution. The values for aluminium chloride are perhaps surprisingly high, but these series were repeated after a considerable interval with similar results. It appears from these results that $N/10$-potassium chloride is not free from surface conductivity on glass. This means that it is not so suitable as hydrochloric or sulphuric acid as a calibrating electrolyte in electro-osmosis determinations as given in Part I of this series. The same may be true to some extent for carborundum, but in any case all the results will be affected in the same ratio. It may be recalled that Stock used 1% sodium chloride solution, which he regarded as a well-conducting salt solution in which the surface conductivity would be negligible.

Experiments were also carried out with dilute alkali, but on account of carbon dioxide contamination the results were untrustworthy. For the same reason probably, the conductivity of $N/10{,}000$-potassium chloride is high.

We hope to give later an account of electro-endosmosis experiments on this same sample of glass. These, in conjunction with the present data, should permit of deductions for the case of electrolytes in a powder diaphragm similar to those made by Stock (*loc. cit.*) for organic liquids.

Determinations of the resistance of carborundum–dilute electrolyte mixtures show that in such circumstances the conductivity of the carborundum is far from negligible.

TABLE II.

*Carborundum.*

| Electrolyte. | Conc. | $R_C$. | $R_B$(calc.). | $R'_B$. | $R'_B/R_B$. |
|---|---|---|---|---|---|
| KCl ..... | $N/10{,}000$ | 13,315 | 10,950 | 8,592 | 0·78 |
| ,, ..... | $N/1{,}000$ | 1,505 | 1,237 | 3,236 | 2·62 |
| ,, ..... | $N/100$ | 158·4 | 130·3 | 468·2 | 3·59 |
| ,, ..... | $N/10$ | 17·35 | 14·27 | 51·96 | 3·64 |
| HCl ..... | $N/1{,}000$ | 519·4 | 427·2 | 1,507 | 3·53 |
| ,, ..... | $N/100$ | 52·8 | 43·4 | 164·8 | 3·79 |
| $AlCl_3$ ..... | $M/1{,}000$ | 707 | 581·5 | 1,855 | 3·19 |
| ,, ..... | $M/100$ | 85·4 | 70·25 | 254·6 | 3·62 |
| Acetic acid ... | $N/1{,}000$ | 4,448 | 3,659 | 6,276 | 1·72 |
| ,, ... | $N/100$ | 1,354 | 1,114 | 3,142 | 2·83 |

In Table II are given the values of the resistances of carborundum powder–electrolyte in cell B. $R_B$, the resistance of cell B containing solution alone, is calculated from $R_C$ and the two cell constants. The surface conductivity is not given, because it is obscured in the more dilute solutions by the conductivity of the carborundum. By plotting the ratio $R'_B/R_B$ against the specific resistance of the solutions, it is found that the carborundum has a specific resistance of the order of $4 \times 10^4$ ohms. This possibly may be due in some slight degree to electrostatic capacity of the carborundum crystals. It is probable that the direct-current resistance as experienced in electro-endosmosis experiments is greater than this alternating-current resistance, on account of polarisation.

The most striking feature of the carborundum experiments was the very large capacity in parallel with the rheostat arm of the bridge necessary in order to obtain a balance. Whereas the cell filled with electrolyte alone, or with electrolyte and glass powder, necessitated an adjustment of only a few micro-microfarads, when it was filled with carborundum powder and electrolyte the capacities were of the order of 0·02 micro-farad (in $N$/10,000-KCl) and 0·05 (in $N$/100-HCl).

Such capacities are unusual with dilute solutions and it was only after some time that the cause of the initial failures to secure a balance was found in a phenomenon due to a kind of "diaphragm polarisation," which appears to occur when various types of heterogeneous diaphragms are interposed between the electrodes in an electrolytic cell. The capacity required also depends on the frequency of the measuring current. In view of its significance in the measurement of the dielectric constant of colloidal systems, this matter is being investigated further. It may be mentioned, however, that the same phenomenon was observed with finely powdered, purified crystalline silicon, powdered graphite, and small pieces of metal in solutions of electrolytes.

*Summary.*

1. The apparent conductivity of several solutions of electrolytes in Jena glass and carborundum powders has been measured.

2. Electrolytes in Jena glass powder show an increased conductivity of several units per cent., the increase being greatest in dilute solutions and least in solutions of strong acids. The increase in the latter case has been assumed negligible, to form a basis of comparison.

3. The alternating-current resistance of carborundum–electrolyte mixtures depends on the conductivity of the electrolyte. In very

dilute solutions, the resistance of the electrolyte becomes of the same order as that of the carborundum.

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## CCCXLIV.—*A New Method for the Preparation of 9-Alkylcarbazoles.*

By HAROLD BURTON and CHARLES STANLEY GIBSON.

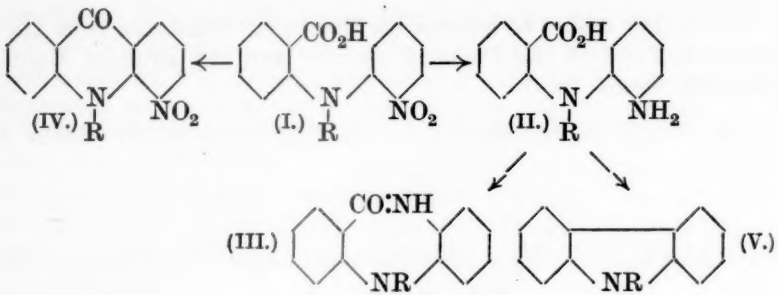
9-ALKYLCARBAZOLES have, in the past, been prepared from carbazole by the ordinary methods of alkylation (Graebe and Behagel, *Annalen*, 1880, **202**, 23; Ehrenreich, *Monatsh.*, 1911, **32**, 1104; Stevens and Tucker, J., 1923, **123**, 2145). During experiments on the synthesis of certain derivatives of diphenylamine we have been able to prepare 9-methyl- and 9-ethyl-carbazole without using carbazole, and this synthesis may have useful applications.

When *N*-methyl-(or ethyl-)anthranilic acid is condensed with *o*-bromonitrobenzene in presence of potassium carbonate and copper powder, the corresponding alkyl 2′-nitrodiphenylamine-6-carboxylic acid (I) is obtained (compare Ullmann, *Annalen*, 1907, **355**, 320). These nitro-acids are readily converted into the amino-acids (II) by the method which has already been described by Clemo, Perkin, and Robinson (this vol., p. 1779). Clemo, Perkin, and Robinson showed that 2′-nitrodiphenylamine-6-carboxylic acid is readily converted into the anhydro-acid or lactam, and we have found that the alkyl derivatives of the same acid also give rise to lactams (III); which is additional proof of the formula given to the lactam by these authors. The lactams described in this paper are also obtained when the acetyl derivatives of the 2′-amino-*N*-alkyldiphenylamine-6-carboxylic acids are heated above their melting points.

When 2′-nitro-*N*-methyldiphenylamine-6-carboxylic acid is heated with concentrated sulphuric acid, most of the acid is recovered unchanged and only a small amount of the 9-nitro-*N*-methylacridone (IV) is obtained. It is clear that the 9-nitroacridone obtained by Clemo, Perkin, and Robinson is formed much more readily from the corresponding acid.

By diazotisation of the above amino-acids and subsequent

treatment with sodium hydroxide, the 9-alkylcarbazoles (V) are obtained in good yield.




## EXPERIMENTAL.

*2′-Nitro-N-methyldiphenylamine-6-carboxylic Acid,* $NO_2 \cdot C_6H_4 \cdot NMe \cdot C_6H_4 \cdot CO_2H$ (I).

—A mixture of methylanthranilic acid (32 g.), *o*-bromonitrobenzene (48 g.), anhydrous potassium carbonate (27·6 g.), amyl alcohol (120 c.c.), and a trace of copper powder was boiled for 4 hours * (compare Ullmann, *loc. cit.*). The volatile substances were removed by steam distillation and, on acidification, the aqueous residue gave a precipitate of crude *2′-nitro-N-methyldiphenylamine-6-carboxylic acid* (41 g.). On crystallisation from ethyl alcohol it was obtained in deep red prisms, m. p. 136—137° (decomp.). 0·2140 gave 19·4 c.c. $N_2$ (moist) at 22°/768 mm.; N = 10·3. $C_{14}H_{12}O_4N_2$ requires N = 10·3%.

*2′-Amino-N-methyldiphenylamine-6-carboxylic acid* (II) was prepared by adding a solution of the nitro-acid (23 g.) in 135 c.c. of 0·880 ammonia and 135 c.c. of water to a hot solution of ferrous sulphate (208 g. in 250 c.c. of water), which was kept stirred during the addition. The product was filtered and the sludge extracted with further quantities of dilute ammonia solution. The whole filtrate was evaporated until crystalline material began to separate, and sulphur dioxide was then passed into the cooled solution until no more acid was precipitated. On reprecipitation from a solution of the ammonium salt, the acid separated in almost colourless crystals, m. p. 130° (decomp.). 0·1979 gave 20·3 c.c. $N_2$ (moist) at 20°/758 mm.; N = 11·8. $C_{14}H_{14}O_2N_2$ requires N = 11·6%.

* Although the condensation of *N*-methyl-(or ethyl-)anthranilic acid with *o*-bromonitrobenzene goes readily in boiling amyl alcohol, we have been unable to condense methylaniline with *o*-bromonitrobenzene under a variety of conditions.

*Anhydro-2'-amino-N-methyldiphenylamine-6-carboxylic Acid* (Lactam) (III).—This compound was prepared in the following ways :

(*a*) by heating 2'-amino-*N*-methyldiphenylamine-6-carboxylic acid above its melting point,

(*b*) by dissolving the amino-acid in boiling xylene, when it separated from the cooling solution,

(*c*) by evaporation of an aqueous solution of the ammonium salt of the amino-acid.

The substance crystallises from xylene or from alcohol in colourless plates, m. p. 213—214°. 0·1706 gave 18·5 c.c. $N_2$ (moist) at 20°/761 mm.; N = 12·6. $C_{14}H_{12}ON_2$ requires N = 12·5%.

*2'-Acetylamino-N-methyldiphenylamine-6-carboxylic acid*,

$$CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe{\cdot}C_6H_4{\cdot}CO_2H,$$

was prepared by heating the amino-acid (5 g.) with acetic anhydride (10 c.c.) on the water-bath for 45 minutes. After removal of the excess of acetic anhydride by steam distillation, the acetyl derivative was separated from a small amount of lactam by extraction with a solution of ammonia and subsequent precipitation with acid. It crystallised from aqueous alcohol in colourless needles, m. p. 194° (decomp.).

The silver salt, prepared in the usual manner, was obtained in colourless plates. 0·2070 gave 0·0572 Ag; Ag = 27·63. $C_{16}H_{15}O_3N_2Ag$ requires Ag = 27·6%.

When the acid (2·84 g.) was heated with glycerol (10 c.c.) for one hour at 210—220°, effervescence took place, and, on pouring the product into a dilute solution of ammonia, a gummy substance separated. This was dissolved in hot alcohol and yielded colourless plates on cooling. The substance melted at 213—214°, alone or mixed with a specimen of the lactam of 2'-amino-*N*-methyldiphenylamine-6-carboxylic acid.

*9-Nitro-N-methylacridone* (IV) was obtained by heating 2'-nitro-*N*-methyldiphenylamine-6-carboxylic acid (10 g.) in 96% sulphuric acid (70 g.) for 3 hours on the water-bath. The solution was poured on to ice, the mixture filtered, and the yellow solid, after thorough washing with water, extracted with hot sodium carbonate solution. The residue (3 g.) crystallised from xylene in yellow prisms, m. p. 176—177°. 0·1481 gave 14·3 c.c. $N_2$ (moist) at 15°/754 mm.; N = 11·26. $C_{14}H_{10}O_3N_2$ requires N = 11·0%.

*9-Methylcarbazole* (V) was obtained by diazotising crude 2'-amino-*N*-methyldiphenylamine-6-carboxylic acid (15·3 g.) in 16·0 c.c. of concentrated hydrochloric acid diluted with 94 c.c. of water, with sodium nitrite (4·8 g.) at 0°. The diazo-solution was made alkaline with cold sodium hydroxide, and the mixture warmed

at 40°. After standing for 12 hours, the crude methylcarbazole (9·4 g.; 82% of the theoretical amount) was filtered off. The solution in ethyl alcohol had the characteristic fluorescence and the compound crystallised from that solvent in long, colourless needles, m. p. 88° (compare Graebe and Behagel, *loc. cit.*).

The picrate crystallised from ethyl alcohol in brick-red needles, m. p. 147° (Graebe and Behagel give 141°) (Found : N = 13·9. Calc., N = 13·7%).

*2′-Nitro-N-ethyldiphenylamine-6-carboxylic acid* (I),

$$NO_2 \cdot C_6H_4 \cdot NEt \cdot C_6H_4 \cdot CO_2H,$$

was prepared in a similar manner to the methyl derivative. It separates from its ethyl-alcoholic solution in yellow prisms, m. p. 135—136°. 0·1776 gave 15·1 c.c. $N_2$ (moist) at 16°/754 mm.; N = 9·9. $C_{15}H_{14}O_4N_2$ requires N = 9·8%.

*2′-Amino-N-ethyldiphenylamine-6-carboxylic acid* (II) was also prepared in the same way as the analogous methyl compound. It had m. p. 98°. The *silver* salt rapidly turns brown on exposure to light. 0·6180 gave 0·1842 Ag; Ag = 29·8. $C_{15}H_{15}O_2N_2Ag$ requires Ag = 29·7%.

*2′-Acetylamino-N-ethyldiphenylamine-6-carboxylic acid*, prepared by the acetylation of the amino-acid, separates from dilute ethyl alcohol in colourless needles, m. p. 145—146°. The *silver* salt is appreciably soluble in water. 0·2130 gave 0·0566 Ag; Ag = 26·6. $C_{17}H_{17}O_3N_2Ag$ requires Ag = 26·6%.

*Anhydro-2′-amino-N-ethyldiphenylamine-6-carboxylic acid* (Lactam) (III) was obtained by methods similar to those for the preparation of the corresponding methyl derivative. The substance separates from alcohol in colourless, flat prisms, m. p. 234—235°. 0·1420 gave 14·8 c.c. $N_2$ (moist) at 18°/749 mm.; N = 12·0. $C_{15}H_{14}ON_2$ requires N = 11·8%.

*9-Ethylcarbazole* (V) was obtained in a 41% yield by diazotisation of 2′-amino-*N*-ethyldiphenylamine-6-carboxylic acid as described for the preparation of 9-methylcarbazole. It crystallised from alcohol in long needles, m. p. 67—68°. The picrate was obtained in crimson needles, m. p. 104—105° (compare Graebe and Behagel, *loc. cit.*) (Found : N = 13·5. Calc., N = 13·2%).

We wish to acknowledge the help of Mr. F. B. Windle, B.Sc., during the experimental portion of this work.

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# CCCXLV.—*The α- and β-Naphthalenesulphonylalanines.*

By William Morris Colles and Charles Stanley Gibson.

In directing attention to the use of β-naphthalenesulphonyl chloride for the identification of amino-acids, Fischer and Bergell described (*Ber.*, 1902, **35**, 3779), among other compounds, β-naphthalenesulphonylalanine prepared from *d*-alanine, but did not record its optical rotatory power. Forster and Fierz (J., 1908, **93**, 1859), who used this reagent for identifying the *d*-alanine obtained by the reduction of ammonium *l*-α-triazopropionate, obtained a β-naphthalenesulphonylalanine having $[\alpha]_D = -57{\cdot}7°$, whilst a specimen prepared from *d*-alanine, isolated from silk, had $[\alpha]_D = -50{\cdot}6°$. In connexion with another investigation, it has been necessary to study for the first time the resolution of the α- and β-naphthalenesulphonylalanines by methods similar to these employed in previous work (Pope and Gibson, J., 1912, **101**, 939; Gibson and Simonsen, J., 1915, **107**, 798). Incidentally, we have been able to determine accurately the constants of the optically active acids and remove the discrepancies which have existed in the case of the β-derivatives.

The resolution of α-naphthalenesulphonylalanine was effected by using first brucine and then strychnine under similar conditions to those employed for the resolution of *p*-toluenesulphonylalanine (Gibson and Simonsen, *loc. cit.*). The brucine salt of the *d*-acid and the strychnine salt of the *l*-acid were readily obtained pure and the pure optically active acids isolated in the usual manner.

The resolution of β-naphthalenesulphonylalanine was effected by separating the strychnine salt of the *d*-acid under conditions similar to those for obtaining the brucine salt of the *d*-α-acid; the crude *l*-β-acid was liberated from the mother-liquor in the ordinary way. The brucine salt of the racemic β-acid having been found to be very sparingly soluble, the crude *l*-β-acid was neutralised with brucine and sodium hydroxide, the amount of the alkaloid being calculated as equivalent to the racemic acid present, leaving the almost pure *l*-β-acid in solution as the sodium salt. After isolation, this *l*-β-acid was converted into the ammonium salt and this only needed one recrystallisation from alcohol for complete purification. The rotatory power of the β-naphthalenesulphonylalanine is opposite in sign from that of the optically active alanine from which it is prepared (Forster and Fierz, *loc. cit.*; Abderhalden and Schittenhelm, *Z. physiol. Chem.*, 1907, **51**, 323).

From our investigation of the pure optically active compounds it is clear that some of the discrepancies in the melting point and other constants of these substances are due to incomplete drying

of the material. The free acids tend to retain moisture most tenaciously. Both the inactive α- and β-naphthalenesulphonylalanines are racemic compounds, and the melting point of the racemate of the α-acid is lower than that of the active forms, whilst the melting point of the β-racemate is higher than that of the corresponding active isomerides. The optical rotatory powers, for the mercury-green line, of the sodium and ammonium salts of the *d*- and *l*-β-naphthalenesulphonylalanines are of the same signs as those of the free acids in alcohol. On the other hand, the rotatory power of the optically active α-naphthalenesulphonylalanine in alcohol and in acetone is opposite in sign to that of the acid in the form of its salts in water. In the form of their salts, the rotatory powers of the optically active β-naphthalenesulphonylalanines are higher than those of the isomeric α-derivatives.

## Experimental.

dl-α-*Naphthalenesulphonylalanine*, $CHMe(NH{\cdot}SO_2{\cdot}C_{10}H_7){\cdot}CO_2H$, described for the first time, is prepared from *dl*-alanine and α-naphthalenesulphonyl chloride under the same conditions as for the preparation of *dl*-β-naphthalenesulphonylalanine. It is readily soluble in ethyl alcohol or ethyl acetate and crystallises in colourless needles, m. p. 133·5°, from much hot water or from benzene (1 g. per 100 c.c.) (0·1280 gave 0·2617 $CO_2$ and 0·0605 $H_2O$; C = 55·7, H = 5·2. $C_{13}H_{13}O_4NS$ requires C = 55·9, H = 4·7%). It is a racemic compound, since its melting point is depressed by admixture with the lævo-isomeride and the melting point of the latter is depressed by admixture with the inactive acid.

dl-β-*Naphthalenesulphonylalanine*, prepared in a 90% yield by following the procedure of Fischer and Bergell (*loc. cit.*), is conveniently recrystallised from a large volume of hot water, but is difficult to obtain free from that solvent. From benzene, in which it is sparingly soluble, it crystallises in small, colourless needles, m. p. 150—150·5° [Found: C = 56·1 (55·9); H = 5·1 (4·7); S = 11·5 (11·5)%]. The acid was also isolated from the brucine salt obtained during the resolution of the externally compensated acid (p. 2508). This was converted into the *ammonium* salt, which crystallised in colourless needles from ethyl alcohol. (0·3332 gave 0·01950 $NH_3$; $NH_3$ = 5·85. $C_{13}H_{16}O_4N_2S$ requires $NH_3$ = 5·74%). On being heated, the ammonium salt begins to decompose at 168°, but its decomposition product has not been investigated.

Like the corresponding α-acid, the β-compound is a racemate, since its melting point is depressed by admixture with the lævo-isomeride and the melting point of the latter is also depressed by admixture with the inactive acid.

*Resolution of* dl-α-*Naphthalenesulphonylalanine.*

This resolution was done twice and the same results were obtained in both cases. In the second experiment, 25·05 g. of the *dl*-acid, 19·3 g. of brucine (0·5 mol.), and 1·1793 g. of sodium hydroxide (0·5 mol.) in standard solution were boiled with 500 c.c. of water, when complete solution took place. The brucine salt of *d*-α-naphthalenesulphonylalanine separated in almost quantitative amount on cooling and was filtered from mother-liquor (*A*). The brucine salt was recrystallised twice, each time from 2 litres of water, but no alteration in rotatory power was observed after the first recrystallisation. It was finally recrystallised from ethyl alcohol (18·6 g. in 100 c.c.).

The *brucine salt of* d-α-*naphthalenesulphonylalanine*,

$$CHMe(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,C_{23}H_{26}O_4N_2,2\tfrac{1}{2}H_2O,$$

was obtained in soft, colourless needles, m. p. 145° [0·5256 lost at 125° 0·0329; $H_2O$ = 6·26 (6·26)%. 0·1369 (anhydrous) gave 0·3206 $CO_2$ and 0·0776 $H_2O$; C = 63·9 (64·2), H = 6·30 (5·83)%]. Its rotatory power * in ethyl alcohol ($c$ = 0·4886, $l$ = 4, $\alpha$ = − 0·24°) was $[\alpha]$ = − 12·3°.

The mother-liquor *A* was made alkaline with ammonia solution and extracted with chloroform until free from brucine. From the aqueous solution, after evaporation to about 50 c.c., the acid was precipitated by a slight excess of hydrochloric acid. The acid (12·3 g.) rapidly crystallised on cooling, and, from a determination of its rotatory power in a solution of sodium hydroxide, it contained 80·5% of the lævo-acid. This acid was mixed with another less pure specimen and finally 14·8 g. of acid containing 75·8% of the lævo-acid were mixed with strychnine (13·4 g., equivalent to the lævo-acid present) and sodium hydroxide (0·5162 g. in standard solution). This required 1500 c.c. of water for complete solution on boiling and the strychnine salt of *l*-α-naphthalenesulphonylalanine separated quantitatively on cooling. After one recrystallisation from 1450 c.c. of water, its rotatory power was constant and not changed by further recrystallisation from aqueous alcohol.

The *strychnine salt of* l-α-*naphthalenesulphonylalanine*,

$$CHMe(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,C_{21}H_{22}O_2N_2,$$

was obtained in colourless iridescent plates from water and colourless needles from aqueous alcohol. The air-dried salt has m. p. 132° [0·1446 (anhydrous) gave 0·3554 $CO_2$ and 0·0797 $H_2O$; C = 67·0 (66·5), H = 6·12 (5·75)%]. Its rotatory power in ethyl alcohol ($c$ = 0·4204, $l$ = 4, $\alpha$ = − 0·33°) was $[\alpha]$ = − 19·63°.

* All rotatory powers were determined at 20° for the mercury-green (5461) line.

*Resolution of* dl-β-*Naphthalenesulphonylalanine.*

As in the previous case, only the second resolution experiment will be described. The *dl*-acid (16 g.) was mixed with 1250 c.c. of water, strychnine (9·6 g.; 0·5 mol.), and sodium hydroxide (1·147 g.; 0·5 mol.). The whole dissolved on boiling and the strychnine salt of the dextro-acid (quantitative) was separated from the mother-liquor (*B*) after cooling. The strychnine salt was pure after one crystallisation from 450 c.c. of ethyl alcohol, but it was again recrystallised from 400 c.c. of the same solvent.

The *strychnine salt of* d-β-*naphthalenesulphonylalanine*,

$$CHMe(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,C_{21}H_{22}O_2N_2,1\tfrac{1}{2}H_2O,$$

was obtained in small, colourless needles, m. p. 197° [0·5210 lost 0·0215 at 125°; $H_2O = 4·13$ (4·2)%. 0·1078 (anhydrous) gave 0·2636 $CO_2$ and 0·0569 $H_2O$; C = 66·7 (66·5), H = 5·86 (5·75)%]. Its rotatory power in ethyl alcohol ($c = 0·4540$, $l = 4$, $\alpha = -0·18°$) was $[\alpha] = -9·94°$.

The acid was isolated from mother-liquor *B* in the usual manner (8·6 g.). A determination of its rotatory power in sodium hydroxide indicated that it contained 40% of the racemic acid. It was mixed with brucine (5·852 g., equivalent to the racemic acid present) and sodium hydroxide (0·7384 g.), and the whole was brought into solution in 900 c.c. of boiling water. The brucine salt of the racemic acid separated in almost quantitative amount on cooling. This was filtered from mother-liquor (*C*) and recrystallised from 800 c.c. of boiling water.

The *brucine salt of* dl-β-*naphthalenesulphonylalanine*,

$$CHMe(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H,C_{23}H_{26}O_4N_2,H_2O,$$

was obtained in long, colourless needles, m. p. 188·5° [0·4566 lost 0·0136 at 125°; $H_2O = 2·98$ (2·60)%. 0·1215 (anhydrous) gave 0·2833 $CO_2$ and 0·0667 $H_2O$; C = 63·6 (64·2), H = 6·10 (5·83)%]. Its rotatory power in ethyl alcohol ($c = 0·4906$, $l = 4$, $\alpha = -0·39°$) was $[\alpha] = -19·9°$. The ammonium salt and also the free acid obtained from this brucine salt were optically inactive. The isolation of pure *l*-β-naphthalenesulphonylalanine from mother-liquor *C* is described below.

*The Optically Active* α-*Naphthalenesulphonylalanines.*

d-α-*Naphthalenesulphonylalanine*, $CHMe(NH\cdot SO_2\cdot C_{10}H_7)\cdot CO_2H$, was obtained from the pure brucine salt by adding an aqueous solution of ammonia, filtering off the precipitated brucine, and extracting the filtrate with chloroform until free from brucine. The aqueous solution was evaporated to small bulk and, on addition of a slight excess of hydrochloric acid, the acid separated as an

oil which rapidly crystallised. After drying, it was recrystallised from benzene (6 g. in 350 c.c.) and obtained in small, colourless prisms, m. p. 141·5—142·5°. The acid is very sparingly soluble in water and readily soluble in ethyl alcohol, ethyl acetate, and acetone [0·1283 gave 0·2649 $CO_2$ and 0·0550 $H_2O$; C = 56·3 (55·9), H = 4·76 (4·69)%]. The following determinations of its rotatory power were made:

In the calculated quantity of $N$/10-NaOH and made up with water:

$c = 0{\cdot}9976$, $l = 2$, $\alpha = +0{\cdot}69°$; $[\alpha] = +34{\cdot}58°$.
$c = 1{\cdot}9992$, $l = 2$, $\alpha = +1{\cdot}63°$; $[\alpha] = +40{\cdot}77°$.

In ethyl alcohol: $c = 0{\cdot}9996$, $l = 4$, $\alpha = -0{\cdot}92°$; $[\alpha] = -23{\cdot}01°$.
In acetone: $c = 1{\cdot}0104$, $l = 4$, $\alpha = -0{\cdot}92°$; $[\alpha] = -22{\cdot}76°$.

l-α-*Naphthalenesulphonylalanine* was obtained from the pure strychnine salt in the usual manner. It was recrystallised from benzene and in its properties corresponded exactly with those of the above *d*-acid; m. p. 141·5—142·5° [0·2161 gave 0·4468 $CO_2$ and 0·0917 $H_2O$; C = 56·4 (55·9), H = 4·75 (4·69)%].

The following determinations of the rotatory power of the acid were made:

As Na salt in water; $c = 0{\cdot}9992$, $l = 2$, $\alpha = -0{\cdot}69°$; $[\alpha] = -34{\cdot}52°$.
In ethyl alcohol; $c = 0{\cdot}9994$, $l = 4$, $\alpha = +0{\cdot}92°$; $[\alpha] = +23{\cdot}01°$.
$c = 4{\cdot}0006$, $l = 4$, $\alpha = +3{\cdot}58°$; $[\alpha] = +22{\cdot}40°$.

In spite of the inconclusive results of experiments undertaken with the object of throwing light on the above interesting reversal in sign of the optical rotatory powers, we hope to obtain further information in connexion with these and closely-related compounds.

*The Optically Active* β-*Naphthalenesulphonylalanines.*

These substances have been previously described (Fischer and Bergell, Forster and Fierz, Abderhalden and Schittenhelm, *loc. cit.*), but they have not been obtained before by the resolution of the inactive acid and there is evidence to show that in some cases the substances as described were not optically pure.

d-β-*Naphthalenesulphonylalanine*,* $CHMe(NH{\cdot}SO_2{\cdot}C_{10}H_7){\cdot}CO_2H$, was isolated in the usual manner from the strychnine salt. The acid crystallised readily and was converted into the *ammonium* salt, which, after one crystallisation from ethyl alcohol, was found to be optically pure. The ammonium salt was obtained in long,

* Described here as "*d*-" because it is dextrorotatory although it has been shown by Forster and Fierz (*loc. cit.*) that *d*-alanine gives rise to the laevo-isomeride.

colourless needles (0·2980 gave 0·01742 $NH_3$; $NH_3$ = 5·84. $C_{13}H_{16}O_4N_2S$ requires $NH_3$ = 5·74%). The rotatory power of the ammonium salt in aqueous solution ($c$ = 0·8100, $l$ = 4, $\alpha$ = + 1·43°) was $[\alpha]$ = + 44·13°. The pure acid was prepared from the pure ammonium salt by decomposing its dilute aqueous solution with standard acid and separated in long, colourless needles which were dried over phosphorus pentoxide for several days and then recrystallised from pure benzene. The melting point altered during the drying and this probably explains the low values obtained by previous workers. The final and constant melting point was 127—128°. Its rotatory power in solution in the calculated quantity of sodium hydroxide gave the following result: $c$ = 2·5028, $l$ = 2, $\alpha$ = + 2·59°, $[\alpha]$ = + 51·74°.

l-β-*Naphthalenesulphonylalanine* was obtained from mother-liquor *C*. The acid was converted into the *ammonium* salt, which had a constant rotatory power after one recrystallisation from ethyl alcohol (0·2032 gave 0·01174 $NH_3$; $NH_3$ = 5·78. $C_{13}H_{16}O_4N_2S$ requires $NH_3$ = 5·74%). The rotatory power of the ammonium salt in aqueous solution ($c$ = 0·8064, $l$ = 4, $\alpha$ = − 1·42°) was $[\alpha]$ = − 44·2°.

The acid, long, colourless needles, obtained from the pure ammonium salt was carefully dried as in the previous case. The melting point rose from 113—114° to a constant value of 127—128°, which was unchanged after the acid had been further recrystallised from pure benzene (1 g. in 30 c.c.) (0·1295 gave 0·2651 $CO_2$ and 0·0578 $H_2O$; C = 55·8, H = 4·96. $C_{13}H_{13}O_4NS$ requires C = 55·9, H = 4·69%). Its rotatory power in ethyl alcohol ($c$ = 1·0010, $l$ = 4, $\alpha$ = − 0·88°) was $[\alpha]$ = − 22·0°.

The rotatory power of the acid in the form of its salts in aqueous solution is of the same sign as that of the acid in ethyl alcohol and no reversal of sign takes place as in the case of the optically active α-acids.

We desire to thank Mr. F. B. Windle, B.Sc., for his help in connexion with a portion of the analytical work.

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# CCCXLVI.—*The Rotatory Dispersive Power of Organic Compounds. Part XIII. The Significance of Simple Rotatory Dispersion. Rotatory Dispersion of Camphorquinone and of Sucrose.*

By Thomas Martin Lowry and Evan Matthew Richards.

Some months ago we presented to the Society a short experimental paper (this vol., p. 1593) in which we showed that octyl alcohol obeyed the law of simple rotatory dispersion, $\alpha = k/(\lambda^2 - \lambda_0^2)$, right up to the limits of accuracy and of range of our observations, but that the oxalate (which nearly obeyed Biot's law) showed systematic deviations which proved definitely that the dispersion was complex. A series of criticisms has since been made of the idea of "simple rotatory dispersion"; and it has even been implied that the discovery of this law has led to a state of chaos rather than of order in the study of rotatory dispersion. It has therefore become necessary to add to the experimental results then recorded some notes on their theoretical significance.

1. *The Simple Dispersion Formula.*

Although Drude put forward in 1898 a general equation for the relation between optical rotatory power and wave-length, he only applied it in the solitary case of quartz, for which he gave the equation $\alpha = 12{\cdot}2/(\lambda^2 - 0{\cdot}010627) - 5{\cdot}046/\lambda^2$. The fact that this equation contains (i) two terms of opposite sign, (ii) a term in which the smaller dispersion-constant was omitted, because its numerical value could not be determined, shows that these are not (as has been suggested) violations of the fundamental principles on which the equation was based. So far as we have been able to find out, however, the equation was not used again, either by Drude himself or by anyone else,* until Lowry and Dickson in 1913 (J., **103**, 1067) discovered that the natural and the magnetic rotatory power of forty-seven organic compounds for seven or eight wave-lengths in the visible spectrum, could be expressed by a single term of the general equation. From that time forward it was clear that the "simple dispersion formula," $\alpha = k/(\lambda^2 - \lambda_0^2)$ (Lowry and Dickson, *Trans. Faraday Soc.*, 1914, **10**, 103), although it was never used by Drude himself, had in fact supplied a new "norm" or standard, with the help of which rotatory dispersions could be tested and classified, just as the even simpler but much less accurate law of inverse-squares was used by Biot, with characteristic prescience,

* Nutting (*Phys. Rev.*, 1903, **17**, 1) used a formula of his own, containing *three* constants in each term.

for the same purpose 100 years before. It is this application of the simple dispersion formula as a means of classifying rotatory dispersions which has now been challenged.

*2. Application of the Simple Dispersion Formula.*

It has been suggested that the classification of rotatory dispersions as simple and complex "is as yet of no practical value" (this vol., p. 1198). This implies a complete misunderstanding of the object with which the present series of investigations was undertaken in 1906. That object was purely utilitarian, namely, to make it possible *to study optical rotatory powers by means of numbers from which the effect of dispersion had been eliminated.* This cannot be done in any case in which the form of the dispersion-curve is not known; and the elimination is neither very easy nor very safe when the dispersion-curve is of a complicated character; but, when a linear relation is found, extrapolation is both simple and accurate. Thus, whenever the simple dispersion formula holds good, the effects of dispersion can be eliminated completely by using the rotation-constant of the one-term equation as a measure of the "absolute rotatory power" of the medium (Lowry and Dickson, J., 1913, **103**, 1067). This involves only a simple linear extrapolation from the longest observed wave-length, *e. g.*, Li 6708, to a wave-length, not very much greater than 10,000 Å.U., at which $\lambda^2 - \lambda_0^2 = 1$ square micron; but no such easy process is yet available for the more complex types of dispersion.

In their fascinating studies of the influence of chemical constitution on rotatory power, Pickard and Kenyon and their colleagues have not made use of the method of extrapolation suggested above, but have arrived at nearly the same result by a process of selection. Thus, most of their optically-active fatty alcohols were found to obey the simple dispersion law, up to the limits within which it could be tested. Many of their esters also conform to the simple law at the lower temperatures, although they begin to deviate from it at higher temperatures (J., 1923, **123**, 14). Even octyl oxalate, which was supplied to us by Dr. Pickard as presenting specially favourable conditions for studying a case of complex dispersion in this series, conforms almost (but not quite) perfectly to Biot's law of inverse squares, so that no serious error would be introduced by a "linear" extrapolation from the observed to the "absolute" rotations. The dispersion-ratios of these fatty alcohols are, moreover, remarkably uniform. *The relative values of their rotatory powers would therefore be almost unchanged by reducing them to absolute rotatory powers,* since the factor for reducing one to the other is approximately the same throughout. In such circumstances

it is obviously possible to eliminate the effects of dispersion almost completely by a judicious choice of materials of similar dispersive power, instead of by making a formal correction.

Similar considerations apply in the case of the sugars, which exhibit (so far as is known at present) a simple and fairly uniform rotatory dispersion (see § 10 below, and *Trans. Faraday Soc.*, 1914, **10**, 103). The notable success of Pickard and his colleagues in unravelling the problem of optical rotatory power in the case of the secondary alcohols, and of Hudson (*J. Amer. Chem. Soc.*, 1909, **31**, 66) and more recently of Maltby (J., 1922, **121**, 2608; 1923, **123**, 1404) in finding simple algebraic relations between the optical rotatory powers of the sugars, are thus seen to depend alike on their selection of compounds of similar rotatory dispersion. It can, however, be asserted with confidence that, when exact mathematical predictions of optical rotatory power can be made, this method of elimination will no longer suffice, and that properly corrected data will have to be used. It is, nevertheless, clear that investigations on these lines are not jeopardised in any way by speculative considerations as to the possible behaviour of the dispersion-curves in the inaccessible ultra-violet region of the spectrum, since the elimination of the influence of dispersion depends on extrapolation to *a region of longer wave-lengths*, where the linear character of the relation between $1/\alpha$ and $\lambda^2$ is not in doubt, and not to the *region of shorter wave-lengths*, where the continued validity of the linear law has been called in question.

3. *Alternative Formulae for Rotatory Dispersion.*

It might be suggested that we are wrong in adhering so rigidly to Drude's equation, *e.g.*, it has been urged that, when two terms of the general equation are used, the four constants might be reduced to two by writing the equation in the form $\alpha = A/\lambda^2 + B/\lambda^4$ (compare J., 1923, **123**, 435, footnote). This is, however, no longer Drude's equation, but the old empirical formula of Boltzmann, which was finally set aside when the correct theoretical form of the equation was discovered by Drude. This formula was tested by Hagenbach (*Z. physikal. Chem.*, 1915, **89**, 570), who plotted $\alpha\lambda^2$ against $1/\lambda^2$ for some 40 of Rupe's compounds, but failed to obtain a linear relation, although 37 out of 40 of these compounds gave an approximate straight line when Drude's formula was submitted to a similar test by plotting $1/\alpha$ against $\lambda^2$.

Boltzmann's equation, like the "simple dispersion formula," contains only *two* constants, and can only be made to fit a curve which can be thrown into the form of a straight line. A *third* constant is therefore obviously required to express the

deviations from a linear law in all cases of complex dispersion, and no difficulty is experienced in calculating accurately this third constant in any equation in which the number of constants is limited to three. It is therefore, as Drude found, the *fourth* constant of the two-term equation, and not the *third*, that is sometimes (but not always) difficult to determine.

4. *Methods of Testing for Simple Rotatory Dispersion.*

The character of a given rotatory dispersion may be tested either by a graphical or by a numerical method.

(a) *Graphical Method.* In his recent paper (this vol., p. 1198), Hunter states that " the method at present adopted for distinguishing between simple and complex rotatory dispersion is a graphical one, which involves plotting $1/\alpha$ against $\lambda^2$." This statement appears to represent correctly his own practice, but it is certainly not ours, which is based upon the view that the graphical method is " the easiest *although perhaps the least exact* method " of testing for simple rotatory dispersion (Lowry and Abram, J., 1919, **115**, 303). We have therefore never used it except as a rough preliminary means of detecting the grosser complexities in the dispersion-curves, as in the case of Rupe's 40 terpene derivatives (*Annalen*, 1915, **409**, 327; J., 1919, **115**, 300), for which only scanty data were available. We should therefore not give to it the same prominence as it receives in Hunter's paper, since, in our opinion, the only valid way of testing the character of a given dispersion-curve is by the numerical method described under (b) below.

(b) *Numerical Method.* This method consists in working out a dispersion formula and then seeing whether a table of observed and calculated rotations exhibits *systematic errors* or only *casual errors*. The suggestion has been made that, in using the numerical method, attention should be concentrated on a small number of wave-lengths, and that the form of the dispersion-curve should be deduced from these, instead of from the long series of wave-lengths which we now employ. Experience has shown, however, that it is impossible to select any short series of, say, four lines, which can be read with sufficient accuracy to give with certainty the correct form of the curve, since a minute error in reading one of the selected lines may easily upset the whole calculation. Thus on two recent occasions the use of four selected readings gave a formula which represented the rotations as rising to infinity and returning again in the interval between two of the lines that had been chosen as standards! It is therefore sheer necessity that has compelled us to impose upon ourselves the task of reading the rotations for *as many wave-lengths as possible*. This method of working is, however,

also vindicated by the fact that, if only a limited amount of time were available for the examination of a compound, more exact results would be obtained by taking a small number of readings of each of a large number of lines, than by taking many readings of a few lines, since the additional accuracy obtained by these extra readings is relatively small. In all crucial cases, however, we have multiplied the number of readings as well as the number of lines, since each of these factors contributes a share to the accuracy of the final results.

(c) *Casual and Systematic Errors.* It has been suggested that we might give the " probable errors " of the readings selected for calculation. The deduction, by mathematical methods alone, of a " probable error " is, however, open to grave objections, since an excellent series of readings, to which a " probable error " of 0·01° might reasonably be assigned, might actually be erroneous to a far greater extent from some unsuspected source of error, such as an unnoticed satellite of the spectrum line used as a source of monochromatic light. The method of working described under (b) above has, however, the great advantage that *the probable errors are compelled to declare themselves*, instead of being deduced from a theoretical formula in which all the main sources of errors are neglected. Thus, whether the equations used to express the curves are regarded as mere interpolation-formulæ, or as disclosing the fundamental constants of the medium, it is clear that exact readings for adjacent wavelengths must at least give a smooth series of " differences " between the observed and calculated rotations. *The fluctuations in these differences are therefore a real measure of the casual errors.* The ability of a given equation to express the readings (up to the limits of accuracy actually attained) can thus be regarded as proved only when the systematic deviations are so much smaller than the casual errors that they can no longer be detected in the table. This result has usually been reached in the formulæ which we have published, although we have been obliged in a few cases to abandon the attempt, because we were unable to express the data by a two-term formula, and were not prepared to undertake the formidable (and generally useless) task of working out a three-term formula to cover them.

5. *Range of Application of the Simple Dispersion Law.*

In deducing his three general dispersion formulæ, Drude made use of a " coefficient of friction $a_h$ " in order to express the damping of the electronic oscillations. He assumed, however, that " the coefficient of friction can be neglected " in the case of " transparent substances " in which " there is no appreciable absorption " of

light. It is in this way that he arrived at the simplified general formulæ for refractive and rotatory dispersion which are now so familiar. In seeking to test these formulæ, it is necessary to accept the limitations imposed by Drude himself, and to apply them only to *transparent substances in which there is no appreciable absorption* of light * of the wave-lengths under consideration. The limitations thus imposed by theory coincide perfectly with those imposed by practical considerations, since optical rotatory powers can be measured with maximum accuracy only by using long columns and high concentrations of the optically active substance, and these can be used only when the substance is highly transparent for light of the range of wave-lengths covered by the experiments. If, in order to secure the transmission of sufficient light, the column is shortened or the concentration diminished, this fact is alone sufficient to suggest that the limits imposed by Drude have been passed, and that a new factor is entering into the measurements and must be taken into account. Any attempt to press the formula further would only be justified in connexion with an investigation (already urgently needed) of the influence of electronic "friction," or whatever the factor may be which prevents the rotatory power from rising to an infinite value on approaching an absorption band.

The importance of Drude's "frictional" terms does not appear to have been generally realised, since we have been criticised on several occasions because our measurements of rotatory dispersion have not been carried sufficiently near to the head of the band. In this connexion, however, the position of the head of the band is far less important than its range; in other words, it is the point at which absorption begins, and not the point at which it reaches a maximum, that determines how far the readings ought to be carried. As an example, camphorquinone has a band, of considerable persistence but no very great intensity, at about 4700 Å.U. and also a "general absorption" which would probably culminate in a band in the Schumann region. But although the two maxima of absorption are separated by over 3000 Å.U., there is no intermediate wave-length at which the compound becomes transparent; and, over the whole range from the green to the furthest ultra-violet, the frictional terms must be allowed for, and the necessary corrections determined (by methods which have not yet been developed) and made, before Drude's equations could legitimately be applied. Since the bands of selective absorption of an organic compound usually cover a range of some hundreds of Ångström units, and may spread over more than

* This condition does not apply to the case of "optically inactive" absorption bands, *e.g.*, to a sugar solution coloured with fuchsine or mauve as in Cotton's experiments (*Ann. Chim. Phys.*, 1896, [vii], **8**, 419).

1000 Å.U. from the head of the band, it is clear that the scope for extending our observations to regions of shorter wave-length is relatively small, and, in particular, is much narrower than the gap between $\lambda_0$ and the smallest value of $\lambda$ recorded in our tables. Indeed, the long exposures which we generally employ for the photographic readings of the shortest wave-lengths are an indication that the permissible limits are already being approached, if not in danger of being actually overstepped, in the observations which we have published.

6. *Partial and Total Rotations.*

In the paper in which the discovery of the validity of the simple formula was described (J., 1913, **103**, 1067) it was pointed out that the rotation of a substance which obeyed the simple dispersion-law up to the existing limits of experimental accuracy might still be " influenced by more than one free period of vibration," and might therefore ultimately be proved to be complex. We have never regarded this fact as any serious drawback to the practical value of the formula, since its chief usefulness is to mark out as suitable materials for further study those compounds which display definite deviations from it. Again, when the terms " simple " and " complex " dispersion were introduced for the first time, at the Faraday Society's General Discussion on " Optical Rotatory Power " in 1914 (Lowry and Dickson, *Trans. Faraday Soc.*, **10**, 96), a case of simple dispersion was described in a compound containing five asymmetric carbon atoms (Lowry and Abram, *ibid.*, p. 103). Each of these atoms had presumably contributed a partial rotation, either positive or negative, to the total rotation of the molecule; but since these partial rotations are probably all controlled by identical or closely similar dispersion-constants, the dispersion was found to conform closely to the simple dispersion law.

In such cases as these, we suggest that the proper course to adopt is (i) to treat as *simple* any dispersion which obeys the simple dispersion law, within the limits described in § 5 above, unless some definite indication of its real complexity can be given; (ii) to regard as *complex* any dispersion which depends on two or more partial rotations, provided that proof can be given, not only that these partial rotations exist, but also that they are controlled by unequal dispersion-constants, since otherwise they would not be able to contribute more than a single term to Drude's equation. This proof need not necessarily depend on directly-observed deviations from the simple dispersion law, since one object of the present paper is to show how indirect evidence can be used for this purpose.

7. *Relation between Dispersion and Absorption.*

In studying the rotatory dispersion of organic compounds we have endeavoured hitherto to keep clear of all subsidiary assumptions, and to make the investigation as far as possible a purely experimental one. For this reason, although we have accepted Drude's equations without reserve, as being valid right up to the limits which he himself imposed, we have always made a point of determining the dispersion-constants of our equations from the dispersions themselves, instead of from other related properties of the medium, such as the selective reflection of infra-red "residual rays" or the refractive dispersion of the medium, both of which were used by Drude in deducing a formula for the rotatory dispersion of quartz. The analysis of the curves can, however, be facilitated by accepting Drude's postulate that the wave-lengths of his dispersion-equations coincide with, and are indeed fundamentally identical with, the wave-lengths of maximum absorption of light, since with the help of this postulate *measurements of absorption* can be used to check the values of the dispersion-constants deduced from *measurements of optical rotatory power* and conversely.

One example of this kind has already been worked out by Pickard and Hunter (J., 1923, **123**, 434) and other examples are now being investigated in the Cambridge laboratory; but our first experiences have shown that the indirect method of determining dispersion-constants is a very dangerous one and should only be applied with the utmost caution. Moreover, it can only be used in cases, such as camphor and camphorquinone, in which the absorption bands are easily accessible in the visible or ultra-violet spectrum. Most of the simpler compounds of which the rotatory dispersions have been measured hitherto are, therefore, outside the present scope of the method, since the absorption bands are either in the inaccessible ultra-violet region, or are submerged beneath a general absorption spreading in from this region, so that they cannot be detected or measured by the methods now in use for studying absortion-spectra. If, however, it is admitted that the characteristic frequency, $1/\lambda_n$, of a partial rotation can be deduced from the observed frequency of the head of an absorption-band, it is clear that the converse proposition must also be admitted, namely, that the position of an inaccessible absorption-band can be deduced by extrapolation from measurements of refractive, magnetic, or rotatory dispersion. An interesting example of this method is afforded by the case of quartz, where the characteristic frequencies lie in a region beyond that investigated by Schumann, but which has been brought within the range of observation by the recent work of Millikan, Fowler, and Simeon, so that a direct experimental verification of Drude's postu-

late by means of ultra-violet "residual rays" may perhaps be possible.

8. *Auxiliary Tests for Simple Rotatory Dispersion.*

(*a*) More than ten years ago, it was pointed out by one of us (J., 1913, **103**, 1075) that a two-term equation with rotation-constants of similar sign would give rise to a curve which would differ only very slightly from a genuine curve of simple rotatory dispersion. This fact was subsequently illustrated (J., 1915, **107**, 1195) by comparing the simple dispersion $\alpha = 1/(\lambda^2 - 0{\cdot}045)$ with the complex dispersion $2\alpha = 1/(\lambda^2 - 0{\cdot}06) + 1/(\lambda^2 - 0{\cdot}03)$, both curves being derived from the two simple dispersions $\alpha_1 = 1/(\lambda^2 - 0{\cdot}06)$ and $\alpha_2 = 1/\lambda^2 - 0{\cdot}03)$ by a process of averaging (in the one case parallel to the axis of $\lambda^2$ and in the other case parallel to the axis of $\alpha$), but with the curious result that one curve is a genuine, and the other is only a false, hyperbola. These two curves run together over a considerable range of wave-lengths, but differ in that the genuine hyperbola rises towards an asymptote of its own at $\lambda^2 = 0{\cdot}045$, whilst the false hyperbola swings aside and rises more steeply to the asymptote $\lambda^2 = 0{\cdot}06$ of one of the parent hyperbolas, and therefore separates more and more widely from its companion as it approaches this asymptote. The views thus put forward anticipate in almost every detail the recently expressed opinions of Hunter (*loc. cit.*) on this subject. Whereas, however, he considers it as practically impossible to distinguish between the two types of curves, we have always regarded it as a difficult problem,* but one which could certainly be solved. We now suggest that one solution of the problem is to be found in using Drude's postulate as the basis of an *indirect* test, to supplement the *direct* tests which we have hitherto used in order to distinguish between simple and complex rotatory dispersion.

(*b*) We have already used an indirect test of a somewhat similar kind, when viewing with suspicion any simple dispersion-equation in which the dispersion-constant for an organic compound is less than the typical minimum value of about $\lambda_0^2 = 0{\cdot}02$; and in the two cases of sodium tartrate and octyl oxalate our suspicions have been fully justified, since the real complexity of the dispersion-curves has been established *by a direct experimental method*, namely, by demonstrating the existence of small but systematic deviations from the simple dispersion law. The indirect method which we now propose to employ is concerned with (and is indeed limited to) those simple or pseudo-simple equations in which the value of the dispersion-constant is not less than about $\lambda_0^2 = 0{\cdot}055$, since it is very

* Experience has proved that the difficulties are much less formidable than we had expected.

difficult at present to make exact measurements of selective absorption beyond $\lambda = 2327$ Å.U. According to the new test, a genuine hyperbolic dispersion-curve can be recognised by the fact that it has as its asymptote the central line of a real absorption-band. On the other hand, a false hyperbola, such as that described above, which is controlled by *two* natural frequencies, will, in the region of longer wave-lengths (in which it imitates most closely the form of a true hyperbola), be directed towards an imaginary asymptote, occupying a position intermediate between the real asymptotes of the component partial rotations.

(*c*) We propose, then, to accept Drude's postulate, in the form in which it is set out in § 7 above, and to admit that the genuineness of a simple dispersion-equation may be challenged by an indirect as well as by a direct method. This admission carries with it, however, an important corollary, namely, that, in the absence of definite evidence to the contrary, a simple dispersion which survives both tests must be accepted as simple. To suggest that all dispersion-curves are complex, and that there is, therefore, probably no such thing as a simple dispersion, is to adopt a purely speculative view, which can only have the effect of discouraging the making of exact measurements in a branch of research where nothing else can be of equal value. The consequent proposal to abandon the distinction between simple and complex dispersion, and to use only the old distinction between normal and anomalous dispersion, is indeed a policy of despair, since it implies that it is useless to attempt to study the mathematical form of the dispersion-curves, and that our resources are exhausted when we have merely noticed whether the rotatory power of a compound increases or diminishes as the frequency of the light increases. In order to prevent misconception, we may add that we have never abandoned the classification of dispersions as normal and anomalous, which is quite different from the distinction between simple and complex dispersion, but on the contrary have placed it on a more secure basis by determining the exact mathematical form of dispersion-curves of both types, and pointing out the essential points of difference between them (J., 1915, **107**, 1195).

9. *Rotatory Dispersion of Camphorquinone.*

The first trial of the new method was made in the case of camphorquinone. In the region of transparency, within which alone Drude's equation is valid, this compound obeys at least approximately the simple dispersion-formula, the value of the dispersion-constant being $\lambda_0^2 = 0{\cdot}2235$, $\lambda_0 = 4730$ Å.U.; that is, if $1/\alpha$ were plotted against $\lambda^2$, we should obtain a straight line directed towards

the point $\lambda = 4730$ Å.U. on the axis of wave-lengths. The observations of Lifschitz (*Z. physikal. Chem.*, 1923, **105**, 27) have shown that, on passing into the region of absorption, the negative rotatory power of this compound rises to a maximum in the middle of the absorption-band, falls to a minimum after passing through it, and then rises again towards a high value of the same sign. In this case, therefore, we had very little doubt that we could establish by our new test the real complexity of the pseudo-simple dispersion.

The first results of the examination were very encouraging. Stewart and Baly had already recorded a strong absorption band at $1/\lambda = 2070$, $\lambda = 4830$ Å.U. The asymptote of our supposedly false hyperbola was at $\lambda = 4730$, a hundred Ångström units beyond this band, and therefore intermediate between the known frequency of the selective absorption in the visible spectrum and the unknown characteristic frequency of the strong general absorption in the ultra-violet. A new series of careful quantitative measurements (this vol., p. 1921) showed, however, that the maximum of absorption was actually *on the other side of our asymptote*, namely at 4650 to 4700 Å.U. This result was disconcerting, since our asymptote appeared to have been displaced in the wrong direction. Further consideration showed, however, that the maximum of selective absorption need not necessarily coincide with the " head " of the band. This would only be true if the selective absorption occurred in a region otside the range of other absorption-bands, and of the general absorption of the compound, so that the peak of selective absorption stood out from a flat plain of zero-absorption. When, however, the selective absorption is superposed on a rapidly increasing general absorption, the values of the latter should first be subtracted from the observed absorption-densities, before plotting the curve of selective absorption; or alternatively, the wave-length of maximum absorption should be determined by drawing a tangent parallel to the slope of the mountain from which the local hummock springs, instead of parallel to the horizon. The magnitude of this correction is not known, but in the case of camphorquinone it would bring the maximum of selective absorption into very close agreement with the asymptote of our dispersion-curve. We have, therefore, no alternative but to regard the hyperbola as genuine, until some new evidence to the contrary is produced.

This result implies nothing more revolutionary than that *the high-frequency partial rotation of camphorquinone has become negligible before the region of transparency is reached*, so that this region is dominated completely by the low-frequency partial rotation. It is perhaps necessary to add that we should be quite ready to admit that this result may be due to secondary causes, such as the cancel-

ling-out of two high-frequency terms, and that, far from wishing to discourage the further study of camphorquinone (on the ground that its simple dispersion is now established beyond dispute), we should welcome any new experimental investigation which would establish the real complexity of the curve.

Other cases now under investigation (mainly on substances exhibiting complex rotatory dispersion) have shown a difference of from 50 to 100 Å.U. between the characteristic frequency of the partial rotation and the frequency of the " head " of the band. The existence of this difference proves that, although measurements of absorption may provide a valuable check upon measurements of rotatory dispersion, they cannot take the place of these measurements, and that the equations of rotatory dispersion can be deduced safely only from the dispersions themselves.

10. *Rotatory Dispersion of Sucrose.*

Another interesting case of a compound which obeys the law of simple rotatory dispersion is sucrose. The sugar, which had been purified by the Bureau of Standards, was made up to a strength of 26 grams per 100 c.c. and was examined in a 6-dcm. tube at 20°. Table I shows that the compound, although it contains nine asymmetric carbon atoms, conforms to the law of simple rotatory dispersion, not only in the visible region, but also in the ultraviolet, as far as we have been able to follow its rotatory power without reducing the length of the column or diminishing the strength of the solution. Thus the average error ($\pm$ 0·05°) in the 18 visual readings is considerably less than the estimated error of about 0·1°, whilst to the 13 photographic readings, which were obtained from exposures not less than a degree apart, may be assigned an estimated error of about half a degree, which is again much larger than the average error (0·2°) actually observed. More important are the facts (i) that the errors are casual and not systematic, and (ii) that the last photographic readings were made with an exposure of 1 hour as compared with $\frac{1}{4}$ hour for light of longer wave-length; but that the deviations in the last three readings are no larger than in those that precede them, in spite of a substantial reduction in the wave-length of the lines. Dilute solutions will transmit light of much shorter wave-length than those used for the last photographic readings; but, in accordance with the views expressed in § 5, we preferred not to put forward, as a test of the applicability of Drude's equation, readings obtained by reducing the concentration or shortening the column of the solution.

An explanation of the simple behaviour of so complex a compound is found in the fact that the nine asymmetric carbon atoms are all

TABLE I.

*Rotatory dispersion of sucrose in aqueous solution* (26 g. in 100 c.c.) *at* 20°.

$[\alpha] = 0{\cdot}641\ a = 21{\cdot}648/(\lambda^2 - 0{\cdot}0213)$.

| Line. | | [α] obs. | [α] calc. | [α] obs.− [α] calc. | Line. | | [α] obs. | [α] calc. | [α] obs.− [α] calc. |
|---|---|---|---|---|---|---|---|---|---|
| Li | 6708 | 50·51 | 50·50 | +0·01 | *Fe* | *4384* | *126·5* | 126·7 | −0·2 |
| Cd | 6438 | 55·04 | 55·05 | −0·01 | *Fe* | *4376* | *127·2* | 127·2 | ± |
| Zn | 6362 | 56·51 | 56·45 | +0·06 | Hg | 4358 | 128·49 | 129·37 | +0·12 |
| Na | 5893 | 66·45 | 66·44 | +0·01 | *Fe* | *4353* | *128·5* | 128·7 | −0·2 |
| Cu | 5782 | 69·10 | 69·16 | −0·06 | *Fe* | *4337* | *129·8* | 129·8 | ± |
| Hg | 5780 | 69·22 | 69·21 | +0·01 | *Fe* | *4315* | *130·7* | 131·3 | −0·6 |
| Cu | 5700 | 71·24 | 71·30 | −0·06 | *Fe* | *4282* | *133·6* | 133·6 | ± |
| Hg | 5461 | 78·16 | 78·18 | −0·02 | *Fe* | *4272* | *134·2* | 134·3 | −0·1 |
| Cu | 5218 | 86·21 | 86·25 | −0·04 | *Fe* | *4261* | *134·9* | 135·1 | −0·2 |
| Cu | 5153 | 88·68 | 88·63 | +0·05 | *Fe* | *4191* | *140·0* | 140·2 | −0·2 |
| Cu | 5106 | 90·46 | 90·44 | +0·02 | *Fe* | *4144* | *144·2* | 143·9 | +0·3 |
| Cd | 5086 | 91·16 | 91·20 | −0·04 | *Fe* | *3889* | *166·7* | 166·7 | ± |
| Zn | 4811 | 103·07 | 103·03 | +0·04 | *Fe* | *3833* | *171·8* | 172·3 | −0·5 |
| Cd | 4800 | 103·62 | 103·53 | +0·09 | *Fe* | *3826* | *173·1* | 173·2 | −0·1 |
| Zn | 4722 | 107·38 | 107·33 | +0·05 | | | | | |
| Zn | 4680 | 109·49 | 109·48 | +0·01 | | | | | |
| Cd | 4678 | 109·69 | 109·58 | +0·11 | | | | | |

The photographic readings are shown in italics.

contained in groups of the type >CH·O—. In two cases this group has the form $\overset{C}{O}$>CH·O·C; in two others, it has the form $\overset{C}{C}$>CH·O·C; in the other five it has the form $\overset{C}{C}$>CH·OH. The dispersion-constant 0·0213 of the simple equation is, moreover, of similar magnitude to those of the simple secondary alcohols. The partial rotations are therefore controlled by dispersion-constants which are either identical or so similar that they would be incapable of producing separate absorption-bands, even if the frequency of the bands were within the range of experimental observation. It is therefore only of speculative interest to consider whether the characteristic frequencies of the different asymmetric carbon atoms (which are joined into two continuous chains by shared electrons) actually synchronise, or vary within narrow limits from atom to atom. Since these variations, even if they exist, could not be detected, either directly by observations of rotatory power, or indirectly by observations of absorption, we propose in this case also to describe the rotatory dispersion as simple, until experimental observations provide evidence of its actual complexity.

11. *Summary.*

(*a*) The meaning of the term "simple rotatory dispersion" is explained and its significance is discussed.

(*b*) An indirect method of distinguishing simple and complex

dispersion by means of measurements of molecular extinction-coefficients is described, and attention is directed to an important source of error which would vitiate any attempt to deduce dispersion-constants from uncorrected observations of absorption.

(*c*) Data are given in reference to the rotatory dispersion of camphorquinone and of sucrose, and their significance is discussed.

We are indebted to the Department of Scientific and Industrial Research for a grant which made it possible for one of us (E.M.R.) to carry out the research described in this paper.

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CAMBRIDGE. [*Received, August 13th,* 1924.]

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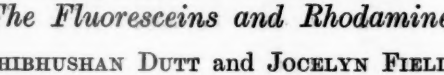
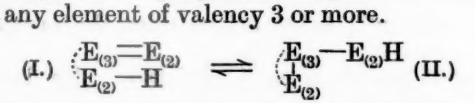
# CCCXLVII.—*Ring-chain Tautomerism. Part XI. The Fluoresceins and Rhodamines.*

By SIKHIBHUSHAN DUTT and JOCELYN FIELD THORPE.

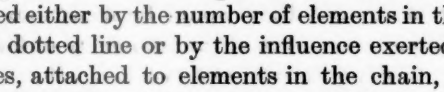
IT has been established in former parts of this series that ring-chain tautomerism may occur between two substances of types (I) and (II), respectively, when $E_2$ represents any element of valency 2 or more and $E_3$ any element of valency 3 or more.



The conditions of tautomerism are primarily determined by the distance apart of the element $E_3$ and the element $E_2$, carrying the mobile hydrogen atom in the open-chain individual (I), and this distance is fixed either by the number of elements in the chain represented by the dotted line or by the influence exerted by groups or ring complexes, attached to elements in the chain, on the carbon tetrahedral angle. Thus it has been established in the case of the monosaccharoses (where $E_3$ = carbon and $E_2$, $E_2$ = oxygen atoms) that tautomerism occurs in water solution under ordinary temperature conditions,



whereas with certain keto-acids (where $E_3$ is carbon and $E_2$ carrying the hydrogen atom in the open-chain form is also carbon) the conditions are such that, when the dotted line represents the three-carbon atom, the deflection of the carbon tetrahedral angle in the manner mentioned above leads to tautomerism of the type



In these cases, however, equilibrium between the individuals is only established in strong alkali at a high temperature.

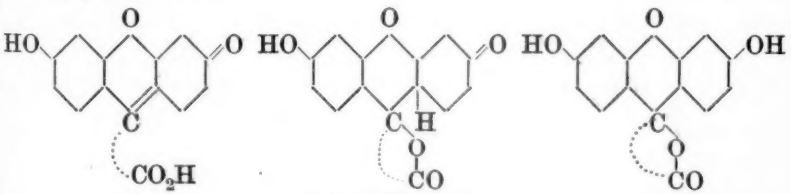
The field of investigation in this subject is obviously a large one, and much more experimental work is needed in connexion with the behaviour of substances containing the various elements of appropriate valency, but having established on a numerical basis the influence of groups and ring complexes on the carbon tetrahedral angle, it seemed desirable to apply these data to certain well-known examples which have not hitherto been recognised as belonging to phenomena of the ring-chain type of tautomeric change. For example, the existence of ring-chain tautomerism in the mutarotatory sugars leads to the conclusion that a simple change will be shown by the system (III)—(IV), or, in other words, that, under

suitable conditions, there will be ring-chain tautomerism between a $\gamma\delta$-unsaturated acid and its $\gamma$-lactone isomeride in solution at the ordinary temperature :

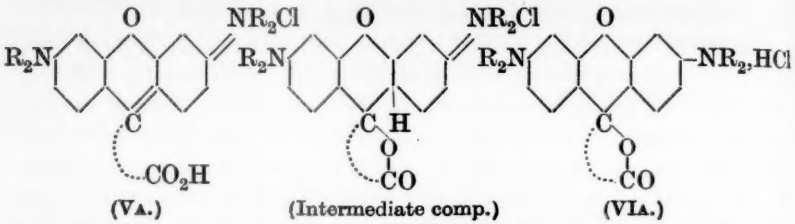
Problems of this kind are now under investigation, but at the same time another series of compounds having a similar structure was studied and this forms the subject of the present communication.

It is now generally recognised that, in the fluoresceins and rhodamines, the change from the colourless base to the coloured salt is accompanied by a change in structure from the lactone to the quinone form, but the precise mechanism of this change has not hitherto been determined. Nevertheless, the assumption of a *para*-linkage in the benzene nucleus along which tautomeric change can be effected is now so necessary—as, for example, in the *p*-nitrosophenols—that it does not require any apology to express this change as taking place through an intermediate form in the following manner :

*The fluoresceins* :



*The rhodamines*:



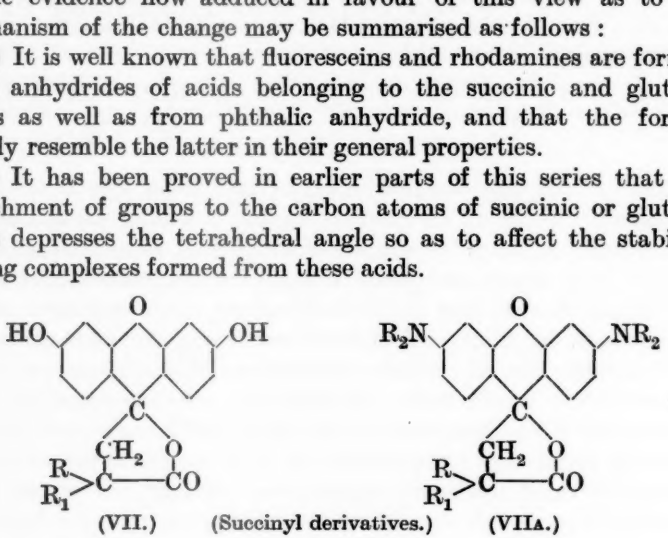
(Va.) (Intermediate comp.) (VIa.)

On this assumption, it follows, therefore, that the change from the lactone to the quinone forms is of precisely the same type as that postulated in the case of the γδ-unsaturated acids and proved to exist in the case of the mutarotatory sugars, being instances of ring-chain tautomerism between the individuals (V) and (VI) and (Va) and (VIa), since it is doubtful whether the intermediate compounds shown have more than a momentary existence.

The evidence now adduced in favour of this view as to the mechanism of the change may be summarised as follows:

(*a*) It is well known that fluoresceins and rhodamines are formed from anhydrides of acids belonging to the succinic and glutaric series as well as from phthalic anhydride, and that the former closely resemble the latter in their general properties.

(*b*) It has been proved in earlier parts of this series that the attachment of groups to the carbon atoms of succinic or glutaric acids depresses the tetrahedral angle so as to affect the stability of ring complexes formed from these acids.



(VII.) (Succinyl derivatives.) (VIIa.)

(VIII.) (Glutaryl derivatives.) (VIIIa.)

(*c*) It follows, therefore, that if our general assumption is correct, there will be a marked difference in the absorption spectra of a series of fluoresceins and rhodamines having the structures (VII) and (VIIA), (VIII) and (VIIIA), such a series having $RR_1$ represented by HH, MeMe, MeEt, EtEt, and the *cyclo*hexane ring; * it also follows that if the stability of the lactone ring is affected by these groups in the two series (succinic and glutaric), it would be evident in the *neutral solution of the base* (phenol) by the fact that the absorption spectra would diminish in intensity in the order given above.

This is clearly evident from the wave-length tables $A_1$ and $A_2$, in which it will be seen that the series of fluoresceins derived from succinic acid, *as*-dimethylsuccinic acid, α-methyl-α-ethylsuccinic acid, *as*-diethylsuccinic acid, and *as-cyclo*hexanesuccinic acid (*cyclo*hexane-1-carboxylic-1-acetic acid), as well as those derived from glutaric acid, ββ-dimethylglutaric acid, β-methyl-β-ethylglutaric acid, ββ-diethylglutaric acid, and β-*cyclo*hexaneglutaric acid (*cyclo*hexane-1 : 1-diacetic acid), all conform to this view. From these experiments, it is evident that there is equilibrium in neutral solution between the lactone and quinone forms and that this equilibrium alters with the alteration of the tetrahedral angle.

(*d*) It follows also, if our hypothesis is correct, that the formation of the alkali salt with, for example, 2 mols. of sodium hydroxide, will stabilise the quinone or coloured form in solution, owing to the formation of the salt of the carboxylic acid, and that the addition of excess of alkali, for example, 20 mols., will lead to the further stabilisation of this form owing to the fact that in weak alkali solution a certain amount of hydrolytic dissociation will undoubtedly occur. Wave-length tables $B_1$ and $B_2$ and $C_1$ and $C_2$ illustrate these points very clearly.

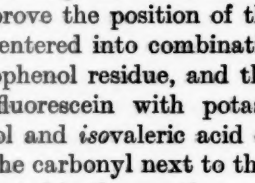
(*e*) The behaviour of a similar series of rhodamines (wave-length

* The name *as-cyclo*hexanesuccinic acid has been given to the acid $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO_2H\\CH_2{:}CO_2H\end{matrix}$, which has hitherto been described as *cyclo*hexane-1-carboxylic-1-acetic acid (Norris and Thorpe, T., 1921, **119**, 1199), because it is only from such a name that it is possible to evolve a reasonable nomenclature for the corresponding fluoresceins and rhodamines. As a systematic name, it is obviously incorrect; but no ambiguity is possible because the acid $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot\underset{CH_2\cdot CO_2H}{CH}\cdot CO_2H$, with which it might be confused, would be called *as-cyclo*hexylsuccinic acid. In the same way, the acid $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\CH_2\cdot CO_2H\end{matrix}$, hitherto called *cyclo*hexane-1 : 1-diacetic acid (Thole and Thorpe, T., 1911, **99**, 422), has been termed *β-cyclo*hexaneglutaric acid.

tables $D_1$ and $D_2$) is clearly in accordance with the general hypothesis; and, finally, in

(*f*) the rhodamine series, it is evident that as the carboxyl group is not affected by the mineral acid which transforms the lactone form into the quinone derivative, the colour must be due to the tendency for the lactone ring to open under the molecular conditions present. Hence, unlike the fluoresceins, they should, if our view is correct, remain practically unaltered as regards their absorption spectra when an excess of mineral acid—for example, 10 mols.—is added. Wave-length tables $E_1$ and $E_2$ clearly show that this is the case.

We consider, therefore, that we have proved our hypothesis as to the nature of the change in the fluoresceins and rhodamines. It was necessary to prove the position of the carbon atom in the succinic series which entered into combination with the resorcinol and *m*-dimethylaminophenol residue, and this was done by fusing the dimethylsuccinylfluorescein with potassium hydroxide; the formation of resorcinol and *iso*valeric acid clearly showed, as was to be expected, that the carbonyl next to the methylene group was the one which participated in the reactions.




## EXPERIMENTAL.

*αα-Diethylsuccinic Acid.*—A mixture of 36 g. of ethyl α-cyano-ββ-diethylacrylate (Birch and Kon, J., 1923, **123**, 2440), 400 c.c. of alcohol, and 15 g. of potassium cyanide in 25 c.c. of water was kept for 2 weeks, when a large quantity of crystalline matter had separated. The alcohol was distilled off and the solution acidified, a heavy oil being precipitated. This oil could not be purified, as it decomposed on distillation in a vacuum, and it was therefore washed with water and hydrolysed by boiling with hydrochloric acid (5 vols.) for 10 hours under reflux. The solution was extracted with ether, the ethereal solution extracted with aqueous sodium carbonate, and the latter acidified, the liberated acid being again taken up in pure ether. On removal of the ether the acid was obtained as an oil which solidified on keeping and was purified by

extracting with light petroleum and recrystallising the residue several times from hydrochloric acid. The pure acid (yield 20%) melts at 108° and closely resembles the *as*-methylethyl acid (Found : C = 55·4; H = 8·3. $C_8H_{14}O_4$ requires C = 55·1; H = 8·0%).

*Preparation of Fluoresceins.*—The condensation of resorcinol with the substituted succinic acids was carried out, using the method described by Biggs and Pope (J., 1923, **123**, 2934) for the preparation of succinylfluorescein.

It was found advantageous in the preparation of the glutaryl-fluoresceins to keep the temperature at 180° for a short time only, until water vapour began to be evolved; it was then maintained at 150—160° for about 2 hours. The colouring matters always contained traces of chlorine unless specially purified by dissolving in sodium carbonate and reprecipitating by means of acetic acid, the precipitate being collected, washed, and dried at 150—160° for 6 hours. All the fluoresceins described in this paper were treated in this way before being used for analysis and spectroscopic work. Glutarylfluorescein was, in addition to this, purified by converting it into the lead lake by means of lead acetate in ammoniacal solution and regenerating the dye with alcoholic sulphuric acid.

The properties of the new compounds obtained are summarised in the tables on pp. 2530–2533.

*Constitution of Dimethylsuccinylfluorescein* (p. 2528).—The colouring matter (15 g.) was gradually added to a mixture of 50 g. of potassium hydroxide and 10 c.c. of water maintained at 180°; the temperature was then gradually raised to 250° and maintained at this point for 1½ hours. The mass was dissolved in water, acidified with sulphuric acid, and distilled in a current of steam until the distillate was no longer acid. The milky distillate was neutralised with sodium carbonate and evaporated to dryness; the white, crystalline solid obtained separated from 90% alcohol in leaflets with a fatty lustre, and proved to be sodium *iso*valerate; this was confirmed by preparing from it the silver salt (Found : Ag = 51·8; calc., 51·6%) and the anilide, m. p. 115° (Found : N = 8·2; calc., 7·9%).

The residue from the steam distillation contained a large quantity of resorcinol; the constitution assigned to dimethylsuccinyl-fluorescein is thus proved.

*Preparation of Rhodamines.*—The method of Farbenfabriken vorm. Fr. Baeyer (D.R.-P. 51983, Friedländer, *Fortsch. Farbenfabr.*, 1891, II, 86) was followed, using a few drops of sulphuric acid as a condensing agent. *cyclo*Hexanesuccinic acid required 4 hours' heating, and glutaric acid even longer; in the latter case a stream of dry hydrogen chloride also was passed through the

*Succinylfluoresceins.*

| Name. Type VII (p. 2526). | Appearance of the product. | M. p. (with decomp.). | Colour of solution in alkali. | Colour in strong sulphuric acid. | Solubility in solvents. | Analysis (calculated values in brackets). |
|---|---|---|---|---|---|---|
| Succinylfluorescein (Resorcinolsuccinein). $RR_1$ = HH. | Pinkish-brown needles with a metallic lustre. | 234° | Red in concentrated, yellow in dilute solution with an intense yellowish-green fluorescence. | Orange-red. | Moderately in alcohol, acetic acid, slightly in ether and water, and insoluble in ligroin. Fairly soluble in hot dilute hydrochloric acid. | — |
| *as*-Dimethylsuccinylfluorescein (Resorcinol-*as*-dimethylsuccinein). $RR_1$ = MeMe. | Long, brown needles with silky lustre. | 262—264° | Do. | Do. | Do. | C = 69·09 (69·2). H = 5·49 (5·4). |
| *as*-Methylethylsuccinylfluorescein (Resorcinol-*as*-methylethylsuccinein). $RR_1$ = MeEt. | Brown, semicircular, radiating needle clusters | 252° | Do. | Orange | Do. | C = 69·59 (69·9). H = 5·5 (5·5). |
| *as*-Diethylsuccinylfluorescein (Resorcinol-*as*-diethylsuccinein). $RR_1$ = EtEt. | Yellow needles. | 262° | Orange in concentrated, light yellow in dilute solution with an intense yellowish-green fluorescence. | Orange-yellow. | Do. | C = 70·4 (70·6). H = 6·0 (5·8). |
| *as-cyclo*Hexanesuccinylfluorescein (Resorcinol-*as-cyclo*hexanesuccinein). $RR_1$ = *cyclo*hexane residue. | Glistening, brown needles. | 278° | Orange in concentrated, light yellow in dilute solution with intense yellowish-green fluorescence. | Yellow. | Do. | C = 72·5 (72·1). H = 6·0 (6·0). |

*Glutaryl fluoresceins.*

| Name. Type VIII (p. 2526). | Appearance of the product. | M. p. (with decomp.). | Colour of solution in alkali. | Colour in strong sulphuric acid. | Solubility in solvents. | Analysis (calculated values in brackets). |
|---|---|---|---|---|---|---|
| Glutarylfluorescein (Resorcinolglutarein). $RR_1$ = HH. | Pinkish-brown needles with metallic lustre. | 235° | Dark red in concentrated, deep yellow in dilute solution with intense yellowish-green fluorescence. | Red. | Moderately in alcohol acetic acid, acetone, sparingly in ether and water and insoluble in light petroleum. Fairly soluble in hot dilute hydrochloric acid. | C = 68·2 (68·4). H = 4·99 (4·6). |
| ββ-Dimethylglutaryl-fluorescein (Resorcinol-ββ-dimethylglutarein). $RR_1$ = MeMe. | Brownish-yellow needles. | 240—245° | Do. | Do. | Do. | C = 69·6 (69·9). H = 5·8 (5·5). |
| ββ-Methylethylglutaryl-fluorescein (Resorcinol-ββ-methylethylglutarein). $RR_1$ = MeEt. | Brown, glistening needles. | 278—280° | Do. | Do. | Do. | C = 70·4 (70·6). H = 5·4 (5·8). |
| ββ-Diethylglutaryl-fluorescein (Resorcinol-ββ-diethylglutarein). $RR_1$ = EtEt. | Yellowish-brown needles. | 162—165° | Red in concentrated, bright yellow in dilute solution with intense yellowish-green fluorescence. | Orange-red. | Do. | C = 71·3 (71·1). H = 6·3 (6·3). |
| β-*cyclo*Hexaneglutaryl-fluorescein (Resorcinol-β-*cyclo*hexaneglutarein). $RR_1$ = *cyclo*hexane residue. | Yellowish-brown, glistening needles. | 238—242° | Orange in concentrated, light yellow in dilute solution with intense yellowish-green fluorescence. | Orange-yellow. | Do. | C = 73·0 (72·6). H = 6·0 (6·3). |

*Succinylrhodamines.*

| Name. (M = *m*-dimethylaminophenol). Type VIIA (p. 2526). | Appearance of the product. | M. p. (with decomp.). | Colour of solution in water or dilute hydrochloric acid. | Solubility in solvents. | Analysis (calculated values in brackets). |
|---|---|---|---|---|---|
| Succinylrhodamine (M-succinein). $RR_1$ = HH. | Hydrochloride - brown needles with golden iridescence and metallic lustre. | 225—230° | Fine bluish-red with bright orange-brown fluorescence. | Fairly soluble in water, but slightly in organic solvents and also in dilute hydrochloric acid. | N = 7·6 (7·4). Cl = 9·5 (9·4). |
| *as*-Dimethylsuccinylrhodamine (M-*as*-dimethylsuccinein). $RR_1$ = MeMe. | Do. | 282—284° | Do. | Do. | N = 7·1 (6·9). Cl = 8·7 (8·8). |
| *as*-Methylethylsuccinylrhodamine (M-*as*-methylethylsuccinein). $RR_1$ = MeEt. | Do. | 260—265° | Do. | Do. | N = 6·5 (6·7). Cl = 8·7 (8·5). |
| *as*-Diethylsuccinylrhodamine (M-*as*-diethylsuccinein). $RR_1$ = EtEt. | Do. | 250—252° | Do. | Do. | N = 6·6 (6·5). Cl = 8·5 (8·2). |
| *as-cyclo*Hexanesuccinylrhodamine (M-*as-cyclo*hexanesuccinein). $RR_1$ = *cyclo*hexane residue. | Free base. Dark reddish-brown needles with golden iridescence. | 110—112° | Do. | Fairly soluble in alcohol, acetone, benzene, moderately in ether, slightly in ligroin, and very soluble in all acids. | N = 6·7 (6·6). |

*Glutarylrhodamines.*

| Name. (M = *m*-dimethylaminophenol). Type VIIIA (p. 2526). | Appearance of the product (free base). | M. p. (with decomp.). | Colour in solution in dilute hydrochloric acid. | Solubility in solvents. | Analysis (calculated values in brackets.) |
|---|---|---|---|---|---|
| Glutarylrhodamine (M-glutarein). $RR_1$ = HH. | Reddish-violet powder. | 190—195° | Fine bluish-red with bright orange-brown fluorescence. | Extremely readily in acids, fairly in alcohol, acetone and benzene, slightly in ether and very sparingly in ligroin. | N = 8·4 (8·0). |
| ββ-Dimethylglutarylrhodamine (M-ββ-dimethylglutarein). $RR_1$ = MeMe. | Fine violet-red needles. | 165—170° | Do. | Do. | N = 7·4 (7·36). |
| ββ-Methylethylglutarylrhodamine (M-ββ-methylethylglutarein). $RR_1$ = MeEt. | Do. | 112—115° | Do. | Do. | N = 7·4 (7·1). |
| ββ-Diethylglutarylrhodamine (M-ββ-diethylglutarein). $RR_1$ = EtEt. | Do. | 120—125° | Do. | Do. | N = 7·0 (6·86). |
| β-*cyclo*Hexaneglutarylrhodamine (M-β-*cyclo*hexaneglutarein). $RR_1$ = *cyclo*hexane residue. | Dark violet-red, glistening needles. | 150—153° | Do. | Do. | N = 6·7 (6·4). |

reaction mixture. The solid mass so obtained was in all cases crushed under water, extracted with dilute ammonia, the residue dissolved in hydrochloric acid, and filtered; the base was then liberated with ammonia, collected, washed, dried, and finally converted into the hydrochloride by dissolving in benzene and then extracting the filtered solution with hydrochloric acid; the hydrochloride crystallised out on evaporating the solution. In cases where the hydrochloride was too soluble to be conveniently purified by this method, the free base, which is insoluble in water, was liberated and purified by crystallisation from dilute alcohol.

In the following tables the figures indicate approximate wavelengths.

TABLE $A_1$.

*Succinylfluoresceins in Alcohol; N*/10,000-solution.

| Thickness of layers in mm. | Position of absorption bands. Succinyl-fluorescein. | Dimethyl S.F. | Methylethyl S.F. | Diethyl S.F. | *cyclo*Hexane S.F. |
|---|---|---|---|---|---|
| 10 | 4867—4552 | 4552—4589 | — | — | — |
| 20 | 4876—4443 | 4622—4430 | 4626—4565 | — | — |
| 30 | 4876—4443 | 4727—4255 | 4626—4565 | — | — |
| 40 | 4901—4443 | 4762—4168 | 4679—4443 | 4613—4527 | — |
| 50 | 4926—4425 | 4762—4157 | 4732—4400 | 4613—4511 | — |
| 100 | 5080 | 4876—3651 | 4802—3726 | 4723—3936 | 4610—4549 |
| 200 | 5088 | 5016 | 5007 | 4845—3612 | 4697—4443 |
| 300 | 5088 | 5026 | 5051 | 4985—3437 | 4758—4409 |
| 400 | 5105 | 5070 | 5063 | 5019 | 4758—4339 |
| 500 | 5105 | 5082 | 5063 | 5048 | 4880—4112 |

TABLE $A_2$.

*Glutarylfluoresceins in Alcohol; N*/10,000-solution.

| Thickness of layers in mm. | Position of absorption bands. Glutaric. | Dimethyl-glutaric. | Methylethyl-glutaric. | Diethyl-glutaric. | *cyclo*Hexane-glutaric. |
|---|---|---|---|---|---|
| 10 | 4552—4430 | 4622—4554 | 4252—4517 | — | — |
| 20 | 4884—4097 | 4832—4144 | 4552—4324 | 4552—4438 | — |
| 30 | 4936—4097 | 4840—3969 | 4840—4105 | 4762—4085 | — |
| 40 | 4058—3992 | 4857—3969 | 4865—4010 | 4865—4010 | — |
| 50 | 5058—3961 | 4902—3812 | 4875—4001 | 4865—4010 | — |
| 100 | 5059 | 4927 | 4937—4014 | 4884—3639 | — |
| 200 | 5079 | 5067 | 5059 | 5059 | — |
| 300 | 5085 | 5075 | 5067 | 5059 | 4622—4552 |
| 400 | 5105 | 5075 | 5067 | 5067 | 4779—4546 |
| 500 | 5162 | 5095 | 5067 | 5067 | 4867—4430 |

## TABLE $B_1$.

*Succinylfluoresceins in Alcohol ; N*/10,000-solution, with 2 molecules of KOH.

Position of absorption bands. Secondary absorptions are given in brackets.

| Thickness of layers in mm. | Succinyl-fluorescein. | Dimethyl S.F. | Methylethyl S.F. | Diethyl S.F. | *cyclo*Hexane S.F. |
|---|---|---|---|---|---|
| 10 | 5001—4552 | 5001—4585 | 5001—4565 | 5020—4937 | — |
| 20 | 5035—4510 | 5025—4552 | 5025—4535 | 5075—4885 | — |
| 30 | 5035—4430 (3650) | 5025—4410 | 5025—4406 | 5095—4625 | 5059—5007 |
| 40 | 5075—4430 (3760) | 5075—4430 | 5075—4425 | 5095—4623 | 5077—4937 |
| 50 | 5075—4365 (3875) | 5075—4430 (3760) | 5075—4425 | 5095—4553 | 5095—4901 |
| 100 | 5185—4165 (3835) | 5135—4110 (3785) | 5095—4185 (3785) | 5050—4185 (3785) | 4935—4265 |
| 200 | 5280—4110 (3965) | 5185—4065 (3865) | 5115—4110 (3865) | 5095—4185 (3865) | 4950—4265 |
| 300 | 5306 | 5145—4015 (3965) | 5135—4085 (3965) | 5095—4110 (3965) | 5010—4185 |
| 400 | 5306 | 5296 | 5135—4015 (4095) | 5035—4085 (4065) | 5050—4185 |
| 500 | 5306 | 5296 | 5135 | 5115—4085 (4075) | 5050—4185 |

## TABLE $B_2$.

*Succinylfluoresceins in Alcohol ; N*/10,000-solution with 20 molecules of KOH.

Position of absorption bands.

| Thickness of layers in mm. | Succinyl-fluorescein. | Dimethyl S.F. | Methylethyl S.F. | Diethyl S.F. | *cyclo*Hexane S.F. |
|---|---|---|---|---|---|
| 1 | 5050—4936 | 5077—4936 | 5073—5013 | — | — |
| 2 | 5075—4884 | 5077—4936 | 5073—4976 | — | — |
| 3 | 5075—4749 | 5077—4901 | 5073—4936 | — | — |
| 4 | 5095—4550 | 5093—4774 | 5073—4936 | — | — |
| 5 | 5095—4550 | 5093—4622 | 5098—4884 | 5059—5015 | — |
| 10 | 5138—4552 | 5138—4552 | 5138—4552 | 5073—4937 | 5059—5007 |
| 20 | 5138—4430 | 5163—4480 | 5163—4552 | 5093—4885 | 5077—4937 |
| 30 | 5164—4395 | 5163—4395 | 5163—4430 | 5093—4623 | 5077—4937 |
| 40 | 5164—4325 | 5197—4365 | 5163—4430 | 5137—4623 | 5095—4901 |
| 50 | 5164—4325 | 5197—4335 | 5193—4335 | 5137—4553 | 5095—4745 |

TABLE $C_1$.

*Glutarylfluoresceins in Alcohol*; $N/10{,}000$-solution, with 2 molecules of KOH.

Position of absorption bands. Secondary absorptions are given in brackets.

| Thickness of layers in mm. | Glutaric. | Dimethyl-glutaric. | Methylethyl-glutaric. | Diethyl-glutaric. | *cyclo*Hexane-glutaric. |
|---|---|---|---|---|---|
| 10 | 5077—4552 | 5077—4555 | 5077—4745 | 5075—4977 | — |
| 20 | 5095—4552 (3306) | 5095—4555 (3306) | 5095—4685 | 5075—4675 | 4935—4885 |
| 30 | 5095—4552 (3760) | 5095—4555 (3760) | 5095—4635 (3306) | 5075—4575 | 4935—4745 |
| 40 | 5115—4465 (3855) | 5130—4555 (3855) | 5095—4535 (3760) | 5080—4575 (3406) | 5077—4745 |
| 50 | 5135—4435 (3915) | 5130—4465 (3915) | 5095—4535 (3855) | 5080—4575 (3855) | 5077—4615 |
| 100 | 5305 | 5305 | 5265—4235 (3915) | 5230—4235 (3915) | 5085—4385 |
| 200 | 5325 | 5325 | 5285—4115 (4035) | 5265—4185 (4035) | 5085—4365 |
| 300 | 5325 | 5325 | 5285 | 5265—4050 | 5085—4365 |
| 400 | 5325 | 5325 | 5305 | 5265 | 5085—4235 |
| 500 | 5325 | 5325 | 5305 | 5265 | 5085—4155 |

TABLE $C_2$.

*Glutarylfluoresceins in Alcohol*; $N/10{,}000$-solution, with 20 molecules of KOH.

| Thickness of layers in mm. | Position of absorption bands. Glutaric. | Dimethyl-glutaric. | Methylethyl-glutaric. | Diethyl-glutaric. | *cyclo*Hexane-glutaric. |
|---|---|---|---|---|---|
| 1 | — | — | — | — | — |
| 2 | — | — | — | — | — |
| 3 | 4997—4937 | 5067—4945 | 5067—4947 | — | — |
| 4 | 5057—4937 | 5067—4945 | 5067—4947 | 5065—4978 | — |
| 5 | 5067—4937 | 5067—4937 | 5067—4947 | 5065—4978 | — |
| 10 | 5077—4552 | 5077—4937 | 5077—4745 | 5077—4947 | — |
| 20 | 4095—4552 | 5095—4552 | 5095—4535 | 5097—4575 | 5077—4937 |
| 30 | 5095—4552 | 5095—4552 | 5095—4535 | 5117—4575 | 5077—4937 |
| 40 | 5115—4465 | 5129—4552 | 5135—4535 | 5129—4575 | 5077—4675 |
| 50 | 5135—4735 | 5129—4465 | 5135—4535 | 5129—4555 | 5077—4665 |

TABLE $D_1$.

*Succinylrhodamines.* Hydrochlorides in water. $N/20{,}000$-solution.

| Thickness of layers in mm. | Position of absorption bands. Succinyl R. | Dimethyl S.R. | Methylethyl S.R. | Diethyl S.R. | *cyclo*Hexane S.R. |
|---|---|---|---|---|---|
| 1 | — | — | — | — | — |
| 2 | — | — | — | — | — |
| 3 | 5555—5465 | — | — | — | — |
| 5 | 5615—5385 | 5555—5465 | 5555—5465 | — | — |
| 10 | 5795—4957 | 5650—5465 | 5625—5450 | 5555—5425 | — |
| 20 | 5750—4753 | 5745—4957 | 5720—5015 | 5650—5325 | 5555—5425 |
| 30 | 5800—4680 | 5800—4850 | 5775—4880 | 5710—5275 | 5650—5465 |
| 50 | 5825—4610 | 5850—4760 | 5830—4737 | 5725—5035 | 5710—5275 |
| 100 | 6015—4450 | 5925—4450 | 5925—4475 | 5835—4534 | 5710—4927 |
| 200 | 6135—3850 | 6135—4306 | 6135—4350 | 5925—4534 | 5825—4534 |
| 300 | 6340 | 6156—3880 | 6156—3880 | 6035—4435 | 5925—4475 |
| 500 | 6375 | 6256 | 6256 | 6135 | 6075 |

TABLE $D_2$.

*Glutarylrhodamines.* Hydrochlorides in water. $N/20{,}000$-solution.

| Thickness of layers in mm. | Position of absorption bands. Glutaric. | Dimethyl-glutaric. | Methylethyl glutaric. | Diethyl-glutaric. | *cyclo*Hexane-glutaric. |
|---|---|---|---|---|---|
| 1 | — | — | — | — | — |
| 2 | — | — | — | — | — |
| 3 | 5555—5435 | — | — | — | — |
| 5 | 5615—5385 | — | — | — | — |
| 10 | 5615—5010 | 5625—5135 | — | — | — |
| 20 | 5675—4835 | 5640—5015 | — | — | — |
| 30 | 5750—4745 | 5725—4957 | 5555—5434 | 5605—5465 | — |
| 50 | 5800—4625 | 5765—4635 | 5685—5250 | 5660—5350 | 5625—5485 |
| 100 | 6050—4384 | 6025—4465 | 5785—4905 | 5785—4534 | 5815—4715 |
| 200 | 6135—4195 | 6125—4235 | 5860—4534 | 5840—4534 | 5850—4685 |
| 300 | 4256 | 6135—3845 | 5880—4450 | 5865—4450 | 5925—4550 |
| 500 | 6340 | 6256 | 6035 | 5995 | 5925 |

TABLE $E_1$.

*Succinylrhodamines.* Hydrochlorides in water, with 10 mols. of HCl. $N/20{,}000$-solution.

Position of absorption bands. Secondary absorptions are given in brackets.

| Thickness of layers in mm. | Succinyl R. | Dimethyl S.R. | Methylethyl S.R. | Diethyl S.R. | *cyclo*Hexane S.R. |
|---|---|---|---|---|---|
| 1 | — | — | — | — | — |
| 2 | — | — | — | — | — |
| 3 | 5555—5465 | 5555—5465 | — | — | — |
| 5 | 5615—5385 | 5615—5410 | 5555—5465 | — | — |
| 10 | 5750—4753 | 5745—4760 | 5650—4927 | 5650—4975 | — |
| 20 | 5800—4658 | 5800—4635 | 5730—4807 | 5710—4865 | 5650—5467 |
| 30 | 5850—4534 | 5850—4560 | 5765—4717 | 5765—4727 | 5650—5435 |
| 50 | 5885—4534 | 5885—4560 | 5810—4625 | 5810—4635 | 5715—4985 |
| 100 | 6256—3850 (3606) | 5925—4421 (3475—3216) | 5925—4435 (3560—3280) | 5925—4465 (3695—3380) | 5875—4534 (3695—3380) |
| 200 | 6340 | 6135—4306 (3505—3006) | 6135—4360 (3505—3006) | 6035—4385 (3560—3006) | 5925—4475 (3560—3006) |
| 300 | 6375 | 6256—3760 (3715—3006) | 6256—3785 | 6195—3885 | 6035—4385 |
| 500 | 6410 | 6280 | 6265 | 6265 | 6135 |

TABLE $E_2$.

*Glutarylrhodamines.* Hydrochlorides in water, with 10 mols. of HCl. $N/20{,}000$-solution.

| Thickness of layers in mm. | Position of absorption bands. Glutaric. | Dimethyl-glutaric. | Methylethyl-glutaric. | Diethyl-glutaric. | *cyclo*Hexane-glutaric. |
|---|---|---|---|---|---|
| 1 | — | — | — | — | — |
| 2 | — | — | — | — | — |
| 3 | 5555—5435 | — | — | — | — |
| 5 | 5615—5385 | — | — | — | — |
| 10 | 5640—4957 | 5625—5035 | — | — | — |
| 20 | 5750—4753 | 5640—4957 | 5625—5465 | — | — |
| 30 | 5765—4625 | 5725—4957 | 5660—5350 | 5625—5465 | 5600—5510 |
| 50 | 5800—4534 | 5765—4585 | 5725—4957 | 5660—5350 | 5625—5465 |
| 100 | 6135—4384 | 6125—4395 | 5860—4534 | 5840—4534 | 5835—4685 |
| 200 | 6256 | 6135 | 5880—4534 | 5865—4534 | 5850—4050 |
| 300 | 6340 | 6256 | 5925—4450 | 5925—4450 | 5925—4585 |
| 500 | 6390 | 6340 | 6135 | 6135 | 6125 |

We are indebted to Professor A. Fowler, F.R.S., for permission to use his spectrograph and to the Research Fund of the Chemical Society for a grant which has partly defrayed the cost of this research.

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SOUTH KENSINGTON. [*Received, July 31st*, 1924.]

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# CCCXLVIII.—*The System Zinc Sulphate–Water.*

By CHARLES R. BURY.

THE earlier measurements of Poggiale, Étard, Mulder, and others are of historic interest only. Callendar and Barnes (*Proc. Roy. Soc.*, 1897, **62**, 147) and Cohen (*Z. physikal. Chem.*, 1900, **34**, 179) have measured accurately, and with close agreement, the solubility of the rhombic heptahydrate, but their data for the solubility of other hydrates are scanty, and it has been found that Cohen misinterpreted the general nature of the system.

## EXPERIMENTAL.

In the earlier part of the work, the usual method was employed : zinc sulphate was shaken with water in a closed tube until it was judged that equilibrium had been attained; the tube was then opened and a sample for analysis withdrawn. Much of the work, however, dealt with unstable hydrates, and a sample could not be withdrawn without the formation of the stable heptahydrate. To overcome this difficulty, suitable quantities of zinc sulphate and water were sealed in V-tubes, made from two $6 \times \frac{1}{2}$ in. test-tubes. These were rotated by a motor in a thermostat until equilibrium had been attained; then the motor was disconnected, and by cautious rotation of a tube by hand, while it remained in the thermostat, it was found possible to transfer all the solid to one limb of the inverted V-tube, leaving a sample of saturated solution in the other. The tube was then withdrawn from the thermostat, dried, and cut in two at the angle. One limb contained the sample for analysis : it was, of course, immaterial if crystallisation of the stable hydrate occurred in the sample, once it had been separated from the solid phase in equilibrium.

At higher temperatures (30—60°), the thermostat was heated by gas; temperatures constant to $\pm 0{\cdot}1°$ were obtained except at the highest temperatures, where the variation occasionally exceeded this limit. At medium temperatures (15—30°), the thermostat was heated and regulated electrically, the variation not being greater than $\pm 0{\cdot}05°$. At lower temperatures, no regulating device

was used; a steady stream of tap water ran into the bath and out through an overflow. Very constant temperatures could be obtained by this method for a period of about 24 hours, when the laboratories were not heated artificially. The actual temperature depended on the time of year.

Determinations at most temperatures were made in duplicate, samples being taken at periods varying from 4 hours to 2 days. Except with the monohydrate, the results agreed satisfactorily, showing that equilibrium was obtained under these conditions. It was found impossible to get any trustworthy results for the monohydrate, as equilibrium was attained so slowly.

All samples were analysed by heating to constant weight in a steam-bath and weighing as $ZnSO_4,H_2O$. This method was employed by Callendar and Barnes and also by Cohen. Preliminary experiments showed the method to be accurate within the limits of the errors of analysis: three determinations gave results agreeing with the theoretical to 1 part in 1000.

The zinc sulphate used was purified from iron, traces of which were found in all commercial samples, and was recrystallised. Distilled water was used.

*Results.*—The solubility of the hexahydrate from 11—61° is shown in Table I: the agreement with Callendar and Barnes's measurements over the range 40—50° is satisfactory. Cohen has measured the solubility from 39° to −5°: his determinations between 39° and 25° only are in agreement with my figures. The rest lie on another curve, and are obviously measurements of the solubility of some other hydrate.

Below 11°, the hexahydrate changes spontaneously and irreversibly to the monoclinic heptahydrate: at about 60° it changes reversibly to another hydrate, probably the monohydrate: much of this remains suspended, forming a milky solution, and does not settle on standing for some hours. Attempts were made to measure its solubility, samples being drawn off through a filter: for example, at 62·8° the solubility (in grams $ZnSO_4$ per 100 $H_2O$) slowly and continuously decreases from 86·0 after 21 hours to 82·2 after 3 days. This slowness in attaining equilibrium and gradual decrease of solubility are probably due to gradual increase in the size of the solid particles, the dimensions of which must approximate to those of a colloid particle, as is shown by their slowness in settling.

The monoclinic heptahydrate is best formed by spontaneous crystallisation of supersaturated solutions at about −10°. Its solubility from 7—23° is shown in Table II; these figures are in close agreement with Cohen's figures for the solubility of the hexahydrate at these temperatures. This hydrate is at all tempera-

tures unstable with respect to the rhombic modification : there is a transition point at $24{\cdot}8 \pm 0{\cdot}3°$, where it is in equilibrium with the hexahydrate.

TABLE I.

Solubility of zinc sulphate hexahydrate.

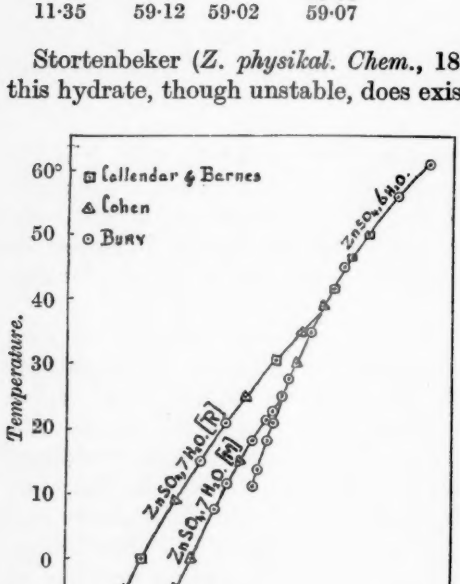
| Temp. | Gms. $ZnSO_4$ per 100 gms. $H_2O$. | | Mean. |
|---|---|---|---|
| 61·1° | 86·1 | 86·3 | 86·2 |
| 56·1 | 81·5 | 81·3 | 81·4 |
| 44·48 | 72·90 | 73·03 | 72·97 |
| 35·03 | 68·10 | 67·90 | 67·98 |
| | 67·92 | 68·02 | |
| 27·63 | 64·46 | 64·47 | 64·46 |
| 25·18 | 63·48 | 63·64 | 63·56 |
| 24·90 | 63·37 | 63·44 | 63·40 |
| 21·02 | 62·03 | 62·17 | 62·10 |
| 18·21 | 61·36 | | 61·36 |
| 13·83 | 59·78 | | 59·78 |
| 11·35 | 59·12 | 59·02 | 59·07 |

TABLE II.

Solubility of zinc sulphate heptahydrate (monoclinic).

| Temp. | Gms. $ZnSO_4$ per 100 gms. $H_2O$. | | Mean. |
|---|---|---|---|
| 22·94° | 62·01 | 62·04 | 62·02 |
| 22·88 | 61·86 | 61·92 | 61·89 |
| 21·56 | 61·10 | 60·86 | 60·99 |
| | 61·00 | 61·01 | |
| 20·90 | 60·41 | | 60·41 |
| 18·23 | 58·94 | 58·91 | 58·93 |
| 11·62 | 54·97 | 55·01 | 54·99 |
| 7·63 | 53·18 | | 53·18 |

Stortenbeker (*Z. physikal. Chem.*, 1897, **22**, 60) has shown that this hydrate, though unstable, does exist, and has obtained a rough measurement of its solubility at 18°. Analysis of some crystals, hastily dried with filter-paper, gave the ratio $ZnSO_4 : H_2O$ as 1 : 7·2 and 1 : 7·3. Measurements of the crystal angles on the goniometer were unsatisfactory, as it was impossible to avoid etching of the faces due to growth of the stable hydrate before the crystal could be dried : the measured angles, however, were close to those of the isomorphous monoclinic ferrous sulphate heptahydrate.




Grams $ZnSO_4$ per 100 gms. water.

*Solubility of Zinc Sulphate.*

A few measurements of the stable rhombic heptahydrate were obtained unintentionally during work on the unstable hydrates : they were in satisfactory agreement with the figures of Callendar and Barnes and of Cohen.

All available data have been used to construct the figure, which shows the solubility of the different hydrates and their transition points.

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ABERYSTWYTH. [*Received, October 28th*, 1924.]

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# CCCXLIX.—*The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. Part IV.*

By WILLIAM MURDOCH CUMMING.

HYDROFERROCYANIDES, precipitated in neutral solution, of the following bases have been prepared (the symbols are defined on p. 1106): Monomethylaniline, $A_3$,B, white plates (s); dimethylaniline, $A_2$,B,2C, white plates (s); *p*-bromodimethylaniline, $A_2$,B,2C, white needles; *p*-nitrosodimethylaniline, $A_4$,B,C, violet plates, and $A_4$,B,7C, precipitated on adding a neutral solution of the hydrochloride to sodium ferrocyanide solution, violet plates (s); *o*-dianisidine, $A_3$,B,4C, pale green plates (s). Benzylamine and methyldiphenylamine formed no salts.

*Hydroferricyanides of the Organic Bases.*—Salts similar to the hydroferrocyanides precipitated in alcoholic solution are formed when freshly prepared alcoholic hydroferricyanic acid is added to absolute-alcoholic solutions of the bases, at −18° if necessary. Salts of primary amines have been obtained in many cases where no such salt was isolated in either acid or neutral solution. The salts, which were as a rule precipitated only by scratching, were washed with absolute alcohol and ether and dried by suction. In some cases, *e.g.*, *o*-anisidine and *p*-xylidine, the alcoholic acid was added directly to the base, as oxidation took place otherwise. Even at −18° serious oxidation took place of the *p*-phenylenediamine, α-naphthylamine, diphenylamine, methyldiphenylamine, and diaminodiphenyl derivatives, nevertheless distinct evidence of salt formation was shown by the microscope in the case of the last.

The salts have similar properties to those already described. They are more soluble in water than the corresponding salts precipitated in acid and neutral solutions. Some of the salts are oxidised on treatment with mineral acids. Salts of hydrazo-compounds were again isolated (see J., 1923, **123**, 2460).

The formulæ, etc., of the salts are given in the following table, B and C representing $H_3Fe(CN)_6$ and $C_2H_6O$, respectively. The compositions were determined as before.

| Base. | Formula. | Crystalline structure, etc. |
|---|---|---|
| Aniline. | $A_3,B,C$ | White plates (s). |
| *o*-Toluidine. | $A_3,B,\frac{1}{2}C$ | Lemon-yellow square plates (s, ss). |
| *m*-Toluidine. | $A_3,B,\frac{1}{2}C$ | Light green plates (s). |
| *p*-Toluidine. | $A_3,B,1\frac{1}{2}C$ | Green plates (s). |
| *o*-Phenylenediamine. | $A_3,B,2\frac{1}{2}C$ | Brown plates. |
| *m*-Phenylenediamine. | $A_2,B,1\frac{1}{2}C$ | Lemon-green plates. |
| Monomethylaniline. | $A_3,B$ | Light green plates (s). |
| Dimethylaniline. | $A_2,B,C$ | Light green plates (s). |
| *p*-Bromodimethylaniline. | $A_2,B,C$ | Green, cubic prisms (s). |
| *p*-Nitrosodimethylaniline. | $A_2,B,C$ | Red, amorphous (s). |
| Pyridine. | $A_3,B,\frac{1}{2}C$ | Lemon-green needles (s, ss). |
| Quinoline. | $A_3,B,\frac{1}{2}C$ | Buff, amorphous (s, ss). |
| *iso*Quinoline. | $A_3,B,\frac{1}{2}C$ | Yellow, amorphous (s). |
| β-Naphthylamine. | $A_3,B,2C$ | Greyish-white plates. |
| Piperazine. | $A_3,B,C$ | Green plates (s). |
| Piperidine. | $A_3,B,C$ | Lemon-green needles (s, ss). |
| Benzylamine. | $A_2,B,1\frac{1}{2}C$ | Silvery plates (s). |
| Hexamethylenetetramine. | $A_2,B,1\frac{1}{2}C$ | Green, amorphous (s). |
| *o*-Anisidine. | $A_4,B,2C$ | Green needles (s). |
| *p*-Xylidine. | $A_3,B,3C$ | Green plates (s, ss). |
| Dimethylaminoazobenzene. | $A_2,B,2C$ | Red plates. |

The difference in solubility of the salts in alcohol enables *o*-toluidine to be separated from *p*-toluidine, and quinoline from *iso*quinoline (compare J., 1922, **121**, 1293; 1923, **123**, 2464). The salts formed by piperidine and β-naphthylamine are soluble in excess of the alcoholic acid and in the case of the latter compound, a yellow sublimate (m. p. 284°) is formed on heating (see J., 1922, **121**, 1295).

*Hydroferricyanides of Hydrazo-compounds.—Hydrazobenzene hydroferricyanide*, $(C_6H_5{\cdot}NH_2{\cdot}N{\cdot}C_6H_5)_2,H_3Fe(CN)_6,4C_2H_6O$, white plates with a blue tinge, is precipitated from a saturated solution of the base; the precipitate dissolves in excess of the acid. The salt fuses slightly even after much washing with absolute alcohol. It is insoluble in boiling water, boiling absolute alcohol, or excess of cold hydrochloric acid, but dissolves in boiling hydrochloric acid, undergoing the benzidine conversion (Found: Fe = 7·34; N = 18·34. Calc., Fe = 7·30; N = 18·25%).

o-*Hydrazotoluene hydroferricyanide*,

$$(C_6H_4Me{\cdot}NH_2{\cdot}N{\cdot}C_6H_4Me),2H_3Fe(CN)_6,C_2H_6O,$$

is precipitated in white plates only after addition of a little ether. Its properties are similar to those described above (Found: Fe = 16·00; N = 27·77. Calc., Fe = 15·82; N = 27·68%).

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# CCCL.—*Tautomerism Depending on the Mobility of a Hydroxyl Group. Part I. Open-chain Triad Systems.*

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THE starting point of this investigation was the suggestion made by Professor Robinson (*Chem. and Ind.*, 1924, **43**, 10) that the mobility of a hydroxyl group might be the cause of the mutarotation of the sugars. So far as sugars and their derivatives are concerned, there can, we think, be no doubt as to the point, because for this theory to cover all cases it would be necessary, not only to postulate a mobile hydroxyl group, but also a mobile amino-group, ethylamino-group, phenylhydrazo-group, etc., and at the same time to exclude arbitrarily the methoxyl group, the dimethylamino-group, and, in fact, all groups which are naturally precluded from giving rise to mutarotation on the mobile-hydrogen theory of Jacobsen and Stelzner.

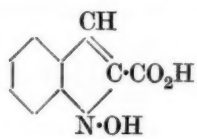
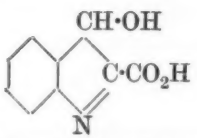
The question raised by Robinson is, however, a wider one, and this investigation was undertaken to ascertain whether a hydroxyl group can become mobile and so give rise to an active tautomeric system (B), analogous to the ordinary triad system (A):

(I.) $[H]X{\cdot}Y{:}Z \rightleftharpoons X{:}Y{\cdot}Z[H]$ (II.) (*System A*)

(III.) $[OH]X{\cdot}Y{:}Z \rightleftharpoons X{:}Y{\cdot}Z[OH]$ (IV.) (*System B*)

(Mobile atoms and groups shown [ ].)

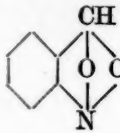
There is already evidence on record which at first sight suggests that irreversible changes at least, of the type (III) → (IV), can occur. Thus Reissert (*Ber.*, 1896, **29**, 646; 1897, **30**, 1045) showed that 1-hydroxyindole-2-carboxylic acid (V) yielded indigotin in presence of a variety of reagents, a reaction most readily explained by supposing that indoxylic acid (VI) is an intermediate product: *

(V.)  →  (VI.)

(a form of indoxylic acid)

* The transformations of geraniol, nerol, and linalool, *e.g.*, by heating with water at 200° (Schimmel & Co., "Handelsberichte," April, 1898, p. 34, and others) are formally similar, although it seems probable that addition products intervene in these cases.

The change (V) → (VI), however, might have another explanation, a bridged-ring compound intervening thus:




The change would then depend on a mobile hydrogen atom and not a mobile hydroxyl group. Indeed, in the general investigation of the system (B), the fact must not be lost sight of that the same results might follow from a combination of ring-chain tautomeric changes:

$$[H]O\cdot X\cdot Y{:}Z \rightleftharpoons X\!<\!\begin{matrix}Y[H]\\ O\end{matrix}\!>\!Z \rightleftharpoons X{:}Y\cdot Z\cdot O[H] \quad (System\ C)$$

It was for this reason * that we decided to examine the system of *N*-hydroxylated amidines (X and Z = nitrogen; Y = carbon), for the hypothetical ring-intermediate corresponding with this series had been already investigated (this vol., p. 87). Moreover, the amidines themselves (System A) are known to be mobile tautomeric substances.

Diaryl *N*-hydroxyformamidines, Aryl·N(OH)·CH:N·Aryl, were originally prepared by Bamberger and his collaborators by the regulated oxidation of di-secondary bases of the type Aryl·NH·$CH_2$·NH·Aryl, and by the dehydration of dihydroxylamines, Aryl·N(OH)·$CH_2$·N(OH)·Aryl (*Ber.*, 1902, **35**, 714, 1874). Neither of these methods, however, indicates the position occupied by the double bond in the product (assuming, for the moment, that it is static), and they are therefore not well adapted to the preparation of pairs of unsymmetrically substituted isomerides (VII and VIII) differing only in the position of the double bond and the hydroxyl group. We therefore decided to utilise the tendency, first noticed by Comstock and Clapp (*Amer. Chem. J.*, 1891, **13**, 528), of methoxymethylene compounds of the type Aryl·N:CH·OMe to condense with hydroxylamine with the elimination of methyl alcohol:

$$Ar\cdot N{:}CH\cdot OMe + NH_2\cdot OH = Ar\cdot N{:}CH\cdot NH\cdot OH + MeOH.$$

By using appropriate β-arylhydroxylamines it was thus possible to prepare the desired isomerides (VII, VIII)

(VII.) Ar·N(OH)·CH:N·Ar′ Ar·N:CH·N(OH)·Ar′ (VIII.)

* And also because a symmetrical system seemed to offer the best chance of observing measurably reversible changes.

The " symmetry test " (Ingold and Piggott, J., 1922, **121**, 2381) showed these compounds to be static. Not only were pairs of isomerides of the types (VII) and (VIII) different from one another, but they were also, apparently, quite non-interconvertible. The " fission test " supported the symmetry test, each isomeride giving rise to its own fission products, and to no trace of those obtainable from the other. The possibility of mobile interchange between individuals of the types (VII) and (VIII), either directly, or by way of a cycloid, appears therefore to be definitely excluded.

A reaction which these results do not exclude, however, is the irreversible decomposition of the cycloid in one or other of the directions depicted in equation *C*. This type of rearrangement has, indeed, been shown to occur. The principal evidence for the ring structure of these compounds was the fact that the same substance could be prepared in the two ways represented by the following equations :

$$\left.\begin{matrix}CH_2{:}NAr\\ O{:}NAr'\end{matrix}\right\} \longrightarrow ArN\!<\!\begin{matrix}CH_2\\ O\end{matrix}\!>\!NAr' \longleftarrow \left\{\begin{matrix}CH_2{:}NAr'\\ O{:}NAr\end{matrix}\right.$$

From this it was inferred that the structure was symmetrical. It is clear, however, that the identity of the products does not necessarily show the symmetry of the structure. The alternatives are, (1) that the substance formed is tautomeric, possessing apparent, but not real, molecular symmetry, (2) that the reactions leading to its formation *pass through* a symmetrical structure. The first of these alternatives has already been disposed of; and it is to the second that we must turn, because the substances obtained in the two ways shown in the equation above are, in each case, identical with one of the pair of isomerides prepared by Comstock and Clapp's reaction. It is clear, therefore, that these cycloids isomerise to hydroxyamidines at the moment of their formation.

Whether a four-membered ring intervenes in Reissert's reaction we have not yet been able to determine, but the evidence, so far as it goes, is in the negative. Examples of the type of ring postulated as intermediate in this case have recently been described (Ingold and Weaver, this vol., p. 1456). These compounds exhibit no tendency towards isomerisation into an open-chain form, although delicate reagents are available for its detection, and it must be inferred that rings of this type are very much more stable than those which yield hydroxyamidines.

As to the existence of a mobile hydroxyl group in a formal triad system, the evidence adduced in this paper is in the negative. The conditions prevailing in analogous dyad systems are now under investigation.

## EXPERIMENTAL.

### (A.) *Formation and Properties of* N-*Hydroxy*-N′-*phenyl*-N-p-*tolylformamidine.*

*Formanilide.*—This substance is best prepared in quantity as follows. Redistilled commercial aniline (273 c.c.) and commercial aqueous formic acid (*d* 1·2) (135 c.c.) were heated together under reflux for ½ hour, and the water was then removed at 100° under diminished pressure. The product, after being allowed to solidify under water, was powdered, left in contact with dilute hydrochloric acid for ½ hour, washed, and dried; the crude substance, although slightly brown, was practically pure (m.p. 46—47°); yield usually about 324 g. (theor. 363 g.).

*Silver Formanilide.*—A filtered solution of the anilide (52 g.) and silver nitrate (62 g.) in 50% alcohol, made up with boiled-out distilled water, was treated very slowly with vigorous shaking, at about 0°, with a 50% aqueous-alcoholic solution of pure sodium hydroxide prepared by dissolving 10 g. of sodium in 120 g. of alcohol and then diluting. The precipitated salt was washed by decantation, dried as completely as possible on porcelain, then finely powdered, further dried at 100° for 1 hour, again powdered, and finally left in an evacuated desiccator. The yield was approximately theoretical, but varied slightly. The salt decomposes on prolonged exposure at 100°, but it is necessary to dry it with the utmost care, as traces of moisture interfere with the subsequent methylation.

*Methoxymethyleneaniline* [*methyl* iso*formanilide*], NPh:CH·OMe, was prepared by keeping a thin paste of the silver salt, methyl iodide (in small excess), and dry ether for 2 days at the ordinary temperature (Comstock and Kleeburg, *Amer. Chem. J.*, 1890, **12**, 497). The silver iodide was washed with dry ether and the combined filtrate and washings were shaken with a little anhydrous calcium chloride to remove any traces of moisture, and then evaporated. The residue on distillation yielded the ether, b. p. 190—200° (32 g. from 108 g. of silver salt), together with a small amount of formanilide, b. p. 265—280° (solidified on cooling).

p-*Tolylhydroxylamine* was prepared by Bamberger's method (*Ber.*, 1895, **28**, 1221).

N-*Hydroxy*-N′-*phenyl*-N-p-*tolylformamidine*, NPh:CH·N(OH)·$C_7H_7$.—A solution in 20 c.c. absolute alcohol of 4·7 g. of *p*-tolylhydroxylamine and 5·15 g. of methoxymethyleneaniline was heated at 50—60° for ½ hour, and hot water was then added until a precipitate began to appear. On cooling, a stiff paste of crystals was obtained, and these were drained and crystallised from dilute alcohol, from which colourless needles, m. p. 151—152° (decomp.), separated

(Found : C = 72·6; H = 6·2. $C_{14}H_{14}ON_2$ requires C = 74·3; H = 6·2. $C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·5%). The analysis shows that either the crystals contain $\frac{1}{3}$ $H_2O$, or they are a mixture of the monohydrated and anhydrous forms. The substance crystallises from benzene with unchanged melting point, but on desiccation for 3 days over sulphuric acid in a vacuum the combined water is removed and the product now crystallises from benzene in colourless, glistening leaflets, m. p. 158° (with blackening and sudden frothing) (Found : C = 74·2; H = 6·2%).

The compound darkens on exposure to light and decomposes perceptibly in the course of several months, even in the dark. Its alcoholic solution gives an intense blue colour with ferric chloride. The copper derivative and hydrochloride are characteristic. On distillation under reduced pressure a liquid distillate is obtained which, treated in alcohol with hydrochloric acid, yields phenyl-*p*-tolylcarbamide. Many attempts were made to convert the hydroxyamidine into the isomeride described in Section B. It was heated with water, dilute acids, and dilute alkalis until decomposition began to set in, but the hydroxyamidine recovered was always identical with the original one.

The *monohydrate* [possibly $NHPh{\cdot}CH(OH){\cdot}N(OH){\cdot}C_7H_7$] was prepared by adding boiling water to an alcoholic solution of the hydroxyamidine until a turbidity was produced, and then boiling off most of the alcohol during about $\frac{1}{2}$ hour. The crystals obtained on cooling separated from dilute alcohol in rosettes of needles, m. p. 142° with very little decomposition (Found : C = 68·9; H = 6·5. $C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·5%).

The *copper* compound, $[NPh{:}CH{\cdot}N(C_7H_7)O{-}]_2Cu$, is precipitated quantitatively when an alcoholic solution of the hydroxyamidine or its hydrate is treated with alcoholic cupric acetate until a blue colour persists in the solution. The chocolate-coloured precipitate is collected, washed, dried, and crystallised from boiling xylene, from which red-brown, silky needles are obtained, m. p. 249° (decomp.).

The *hydrochloride*, $NPh{:}CH{\cdot}N(OH){\cdot}C_7H_7,HCl$, may be obtained by digesting the copper salt, or the hydrate, or the amidine itself, with warm 15% hydrochloric acid, but is best prepared by adding concentrated hydrochloric acid to an alcoholic solution of the amidine, or its hydrate, when colourless needles separate, which, after crystallisation from glacial acetic acid, melt at 196° (decomp.) (Found : C = 64·1; H = 5·8. $C_{14}H_{15}ON_2Cl$ requires C = 64·0; H = 5·7%).

*Decomposition of* N-*Hydroxy*-N′-*phenyl*-N-p-*tolylformamidine by means of Alkalis : Formation of* p-*Azoxytoluene, Formic Acid, and*

*Aniline.*—The hydroxyamidine was boiled with aqueous-alcoholic 8% sodium hydroxide for 2 hours, the alcohol removed by evaporation, and a little charcoal added. The filtered solution was strongly acidified and extracted with ether (a), then made alkaline and again extracted (b). The aqueous residue (c) was saturated with carbon dioxide and once more extracted with ether. This extract on evaporation gave an amphoteric substance which had the properties of an aminophenol, and was probably the unknown 4-amino-*m*-cresol, but it could not be purified on account of its tendency to become oxidised.

p-*Azoxytoluene.*—The acid extract (a) on evaporation left a red oil having the odour of formic acid. On boiling with water and cooling, the insoluble portion set to a paste of crystals, which, on draining and crystallising from alcohol, yielded pure azoxytoluene, m. p. 75° (identified by direct comparison and a mixed m. p. determination).

From the aqueous residue (c), neutralised with sodium hydroxide, sodium formate was obtained.

The ethereal extract (b) was evaporated and the residue distilled and identified as aniline by the usual tests, and by conversion into benzanilide by the Schötten-Baumann method. The benzanilide was pure and contained no trace of benzo-*p*-toluidide.

(B). *Formation and Properties of* N-*Hydroxy*-N-*phenyl*-N′-p-*tolylformamidine.*

Formo-*p*-toluidide was prepared from 107 g. of *p*-toluidine and 45 c.c. of commercial formic acid (*d* 1·2) as in the case of formanilide, excepting that it was found advisable to omit the half-hour's heating under reflux. The yield of the crude dried product, m. p. 52°, was 122 g. (theoretical 135 g.).

The *silver* salt was prepared, as in the case of the aniline derivative, from 40 g. of the toluidide, 43 g. of silver nitrate, and 6·8 g. of sodium.

*Methoxymethylene*-p-*toluidine* [*methyl* iso*formo*-p-*toluidide*], $N(C_7H_7)$:CH·OMe, b. p. 214—218°, was prepared like the aniline derivative, 18 g. being obtained from 63 g. of the silver salt. This preparation appears even more sensitive to traces of water than the analogous one described in Section A, and it is desirable to employ " Grignard " ether as diluent.

*Phenylhydroxylamine.*—The methods described in the literature for the preparation of this substance are for the most part either difficult to carry out, or uncertain in their results. A mixture of nitrobenzene (40 c.c.) and 400 c.c. of water containing 24 g. of ammonium chloride was shaken vigorously and immediately mixed

with 72 g. of zinc dust. The shaking was continued without intermission for about 20 minutes, much heat being evolved. The mixture was then filtered, the precipitate washed with a very little water, and the combined filtrates were immediately cooled, saturated with sodium chloride, and cooled to 0°. The hydroxylamine was collected, dried on porcelain, and crystallised from benzene. The yield varies slightly, but is close to 20 grams.

N-*Hydroxy*-N-*phenyl*-N′-p-*tolylformamidine*, $N(C_7H_7){:}CH{\cdot}NPh{\cdot}OH$, was prepared from 10·5 g. of the methoxymethylene compound and 7·7 g. of phenylhydroxylamine by condensation in alcoholic solution at 50—60°, as in the analogous reaction described above. The crystalline product, leaflets which quickly turn green on exposure to light, melted at 130—140° with very little decomposition, and crystallisation from dilute alcohol or benzene did not appreciably change this m. p. (impure hydrate). After drying for 3 days over sulphuric acid in a vacuum, and then crystallising from benzene, leaflets were obtained, m. p. 151° with sudden decomposition and frothing (Found: C = 74·0; H = 6·3. Calc., C = 74·3; H = 6·2%). This substance is identical with that previously described as phenyltolylmethyleneoxadi-imine (*loc. cit.*).

This substance is very similar in properties to its isomeride (Section A); a mixture of the two melts below 140°. All attempts which were made to convert it into its isomeride of m. p. 158° by heating with water, acids, and alkalis were unsuccessful. On distillation under reduced pressure a liquid distillate is obtained which yields phenyl-*p*-tolylcarbamide on treatment with aqueous-alcoholic hydrochloric acid.

The *monohydrate* [possibly $NH(C_7H_7){\cdot}CH(OH){\cdot}NPh{\cdot}OH$], clusters of needles, m. p. 138°, was prepared like its isomeride; a mixture of the two shows a large depression of m. p. (Found: C = 68·7; H = 6·5. $C_{14}H_{16}O_2N_2$ requires C = 68·9; H = 6·5%).

The *copper* compound $[N(C_7H_7){:}CH{\cdot}NPh{\cdot}O—]_2Cu$, prepared like its isomeride, separates from xylene in small, red-brown needles, m. p. 253° (decomp.). A mixture of the two isomerides melts at about 200° (Found: C = 65·25; H = 5·1. $C_{28}H_{26}O_2N_4Cu$ requires C = 65·4; H = 5·1%).

The *hydrochloride*, $N(C_7H_7){:}CH{\cdot}NPh{\cdot}OH,HCl$, prepared like its isomeride, separated from glacial acetic acid in glistening blades, m. p. 200° (decomp.) (Found: C = 64·0; H = 5·9. $C_{14}H_{15}ON_2Cl$ requires C = 60·4; H = 5·7%).

*Decomposition of* N-*Hydroxy*-N-*phenyl*-N′-p-*tolylformamidine by Alkalis: Formation of Azoxybenzene, Formic Acid, and* p-*Toluidine.*—The decomposition was carried out as described in Section A, and the neutral, acid, basic, and amphoteric products were separated.

The neutral oil, which could not be induced to crystallise, was heated with iron filings; the distillate, on rubbing with dilute hydrochloric acid, yielded pure azobenzene. The neutral oil must therefore have consisted essentially of azoxybenzene, and could have contained no trace of azoxytoluene.

The basic product readily crystallised, and was identified as *p*-toluidine (by direct comparison and by conversion into benzo-*p*-toluidide); no benzanilide could be detected.

The acid product was identified as formic acid as before.

The amphoteric product probably consisted essentially of *p*-aminophenol, but the quantity was too small to admit of proper purification.

(C.) *Formation and Properties of* N-*Hydroxy*-N-*p-chlorophenyl*-N′-p-*bromophenylformamidine.*

Formo-*p*-bromoanilide, prepared from ethyl formate and *p*-bromoaniline by Dennstedt (*Ber.*, 1880, **13**, 234), can most readily be made as follows: *p*-Bromoaniline (86 g.) is heated under reflux with 73 c.c. of formic acid (*d* 1·2) until the liquid has separated into two layers (prolonging the heating leads to rapid decomposition), the water is removed at 100° under reduced pressure, and the solid product crushed under dilute hydrochloric acid and dried as formerly. The yield is almost theoretical.

The *silver* salt was prepared as previously described from 30 g. of formo-*p*-bromoanilide, 25·5 g. of silver nitrate, and 3·45 g. of sodium. It forms white needles which darken slowly in light whilst wet, but if dry appear to be quite stable (Found: Br = 25·6. $C_7H_5ONBrAg$ requires Br = 25·1%).

*Methoxymethylene*-p-*bromoaniline* [*Methyl* iso*Formo*-p-*bromoanilide*], $C_6H_4Br{\cdot}N{:}CH{\cdot}OMe$.—By the procedure used in the previous methylations, 26 g. of a colourless oil, b. p. 245—250°, were obtained from 46 g. of silver salt and 10 c.c of methyl iodide. On redistillation, almost the whole boiled at 245—246° (Found: Br = 37·5. $C_8H_8ONBr$ requires Br = 37·6%).

p-*Chlorophenylhydroxylamine* was prepared by reduction of *p*-chloronitrobenzene (13·5 g.) with 5% zinc amalgam (500 g.) in 400 c.c. of a boiling 50% aqueous-alcoholic solution of aluminium sulphate (24 g.) (compare Bamberger and Knecht, *Ber.*, 1896, **29**, 864). The product was crystallised from dilute alcohol (yield 6 g.); m. p. 87—88°.

N-*Hydroxy*-N-p-*chlorophenyl*-N′-p-*bromophenylformamidine*, $C_6H_4Cl{\cdot}N(OH){\cdot}CH{:}N{\cdot}C_6H_4Br$.—An absolute-alcoholic solution of 3·2 g. of methoxymethylene-*p*-bromoaniline and 2·14 g. of *p*-chlorophenylhydroxylamine was heated on the water-bath at 60° for

½ hour or until crystals (yellow needles) ceased to be deposited. After cooling, 3 g. of solid were collected, dried, and crystallised from a large volume of boiling benzene, from which almost colourless needles separated, m. p. 171° (instantaneous decomposition and frothing). A further quantity was obtained from the alcoholic mother-liquors by adding water and crystallising the dried precipitate from benzene (Found: C = 48·0; H = 3·2. Calc., C = 47·9; H = 3·1%).

Direct comparison showed this substance to be identical both with the addition product of *p*-chloronitrosobenzene with methylene-*p*-bromoaniline, and with the addition product of *p*-bromonitrosobenzene and methylene-*p*-chloroaniline. It is, however, markedly different from the isomeride described in Section D, for instance, in its slight solubility in boiling benzene, and in the fact that it exhibits no tendency to form a hydrate. It gives a deep blue colour with ferric chloride. After keeping for several months, it shows signs of decomposition.

The *copper* derivative, $[C_6H_4Br\cdot N{:}CH\cdot N(C_6H_4Cl)\cdot O\cdot]_2Cu$, is precipitated quantitatively from an alcoholic solution when a slight excess of alcoholic copper acetate is added. It separates from boiling xylene in small, silky, maroon-coloured needles, m. p. 275° (decomp.) (Found: C = 43·7; H = 2·5. $C_{26}H_{18}N_4Cl_2Br_2Cu$ requires C = 43·8; H = 2·5 %).

The *hydrochloride*, $C_6H_4Cl\cdot N(OH)\cdot CH{:}N\cdot C_6H_4Br,HCl$, tiny, colourless leaflets, m. p. 260° (decomp.), is best prepared by the addition of hydrochloric acid to a warm alcoholic solution of the base, and may be crystallised from glacial acetic acid (Found: C = 43·4; H = 2·9. $C_{13}H_{10}ON_2Cl_2Br$ requires C = 43·3; H = 2·8%).

All attempts to prepare the hydrate of the base were unsuccessful.

pp′-*Dichloroazoxybenzene* can readily be isolated from the benzene mother-liquors obtained in crystallising the hydroxyamidine, if these are combined and evaporated, and the portion of the residue easily soluble in cold benzene is crystallised from a mixture of this solvent with ligroin. It was identified by direct comparison and a mixed m. p. determination (155°) with an authentic specimen.

*Decomposition of* N-*Hydroxy*-N-p-*chlorophenyl*-N-p-*bromophenylformamidine by Alkalis: Formation of* pp′-*Dichloroazoxybenzene*, p-*Bromoaniline, and Formic Acid.*—This reaction was carried out like those previously described, and the neutral, basic, acid, and amphoteric products were separated similarly. The *pp*′-dichloroazoxybenzene obtained from the neutral fraction, which at once solidified, was unaccompanied by any dibromoazoxybenzene. The *p*-bromoaniline isolated from the basic fraction (also solidified)

contained no trace of *p*-chloroaniline. The acid fraction consisted of formic acid (identified as usual), but the amphoteric substance resisted all attempts to purify it.

(D.) *Formation and Properties of* N-*Hydroxy*-N′-p-*chlorophenyl*-N-p-*bromophenylformamidine.*

Formo-*p*-chloroanilide, obtained by Chattaway, Orton, and Hartley by isomerisation of *N*-chloroformanilide (*Ber.*, 1899, **32**, 3636), is best prepared in the same way as the bromo-compound, the same precautions being observed; m. p. 100—102° (recorded m. p. 102°); the yield was 68 g. from 64 g. of *p*-chloroaniline and 23 c.c. of commercial formic acid (*d* 1·2).

The *silver* salt was prepared like the preceding one from 30 g. of *p*-chloroaniline, 32·8 g. of silver nitrate and 4·45 g. of sodium. It had similar properties (Found: Cl = 13·4. $C_7H_5ONClAg$ requires Cl = 13·5%).

*Methoxymethylene*-p-*chloroaniline* [*Methyl* iso*Formo*-p-*chloroanilide*], $C_6H_4Cl{\cdot}N{:}CH{\cdot}OMe$.—By the method previously used, 26 g. of a colourless oil, b. p. 230—235°, were obtained from 46 g. of the silver salt and 10 c.c. of methyl iodide. On redistillation, almost the whole boiled at 230—231° (Found: Cl = 21·1. $C_8H_8ONCl$ requires Cl = 20·9 %).

*p*-Bromophenylhydroxylamine was prepared like the chloro-compound, using, however, 17·2 g. of *p*-bromonitrobenzene, the other quantities being the same as before (yield 5 g.); m. p. 88°.

N-*Hydroxy*-N′-p-*chlorophenyl*-N-p-*bromophenylformamidine*, $C_6H_4Br{\cdot}N(OH){\cdot}CH{:}N{\cdot}C_6H_4Cl$.—This was prepared by condensing 3·2 g. of methoxymethylene-*p*-chloroaniline with 4 g. of *p*-bromophenylhydroxylamine in absolute alcohol at 60°, as described for the isomeride; but no crystals separated from the hot solution in this case. The small deposit obtained on cooling consisted essentially of the hydroxyamidine, which, after crystallisation from benzene, melted at 168° with vigorous decomposition. Most of the material was, however, obtained in the form of hydrate (mixed with some *pp′*-dibromoazoxybenzene) by adding water to the alcoholic solution (Found: C = 47·8; H = 3·1. $C_{13}H_{10}ON_2ClBr$ requires C = 47·9; H = 3·1%).

This substance, unlike its isomeride, is easily soluble in hot benzene, and combines with water readily to form a very stable hydrate. It gives the normal deep blue colour with ferric chloride.

The *hydrate* [possibly $C_6H_4Br{\cdot}N(OH){\cdot}CH(OH){\cdot}NH{\cdot}C_6H_4Cl$] is also obtained by digesting the hydroxyamidine with water, and separated from admixed dibromoazoxybenzene by extracting with cold 80% alcohol; recrystallised from more dilute alcohol, it forms

small clusters of needles, m. p. 144—145° (Found: C = 45·3; H = 3·4. $C_{13}H_{12}O_2N_2ClBr$ requires C = 45·4; H = 3·5%). The hydrate is extremely difficult to dehydrate, being unaffected by several weeks' exposure in a vacuum desiccator over sulphuric acid. Partial dehydration is effected when it is left in the steam-oven until deep-seated decomposition begins to occur; the product is crystallised several times from benzene.

The *copper* derivative, $[C_6H_4Cl\cdot N{:}CH\cdot N(C_6H_4Br)\cdot O\cdot]_2Cu$, prepared as before, crystallises from boiling xylene in chocolate-brown needles, m. p. 255° (decomp.) (Found: C = 43·6; H = 2·6. $C_{26}H_{18}O_2N_4Cl_2Br_2Cu$ requires C = 43·8; H = 2·5%).

The *hydrochloride*, $C_6H_4Br\cdot N(OH)\cdot CH{:}N\cdot C_6H_4Cl,HCl$, prepared like its isomeride, crystallises from glacial acetic acid in pearly leaflets, m. p. 295° (decomp.) (Found: C = 43·2; H = 2·9. $C_{13}H_{10}ON_2Cl_2Br$ requires C = 43·3; H = 2·8%).

pp′-*Dibromoazoxybenzene.*—This was separated from the above hydrate by taking advantage of its small solubility in cold 80% alcohol, and its great solubility in cold benzene. It was finally crystallised from a small amount of benzene, and identified by direct comparison and a mixed m. p. determination (172°) with a genuine specimen.

*Decomposition of* N-*Hydroxy*-N′-p-*chlorophenyl*-N-p-*bromophenylformamidine by Alkalis: Formation of* pp′-*Dibromoazoxybenzene*, p-*Chloroaniline, and Formic Acid.*—This decomposition was carried out (using the hydroxyamidine hydrate) like that described in Section A, and the neutral, acid, basic, and amphoteric products were separated in the same way. The neutral fraction, which solidified, yielded *pp′*-dibromoazoxybenzene unaccompanied by any dichloroazoxybenzene; the acid product consisted of formic acid; the basic part, which also solidified, gave *p*-chloroaniline unaccompanied by any *p*-bromoaniline. The amphoteric product contained halogen, and gave the usual tests for primary bases and phenols, but it could not be purified.

We wish to thank the Chemical and Royal Societies for grants by the aid of which the expenses of this investigation have been met.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, August 15th,* 1924.]

# CCCLI.—*The Complexity of the Solid State. Part I. The Behaviour of Pure Sulphur Trioxide. Part I.*

By Andreas Smits and Pieter Schoenmaker.

## *Introduction.*

It has already been suggested by one of the authors (Smits, *Ber. Sächs. Akad. Wiss. Leipzig*, 1923, **75**, 58) that sulphur trioxide should be a promising material for testing the theory of allotropy.

Marignac (*Arch. Gen.*, 1853, **22**, 225; 1875, **52**, 236) was the first to state that sulphur trioxide appears in two solid forms, an ice-like α (m. p. 17°) and a silk- or asbestos-like β, the latter not melting under atmospheric pressure but giving a vapour from which the α-form condenses.

According to Schultze and Sellac (*Bull. Soc. chim.*, 1870, **14**, 154; *Ber.*, 1870, **3**, 215), the liquid obtained from sulphur trioxide (m. p. 16°) sometimes contained white flakes, out of which, below 25°, fine white needles grew, leading ultimately to the complete crystallisation of the liquid. In sealed tubes, this needle-like form melted over the range 50° to 80°; at 20°, it had a vapour pressure which was inappreciable at first, but rose in 8 days to 30—40 mm. of mercury.

Reference may also be made to the work of Weber (*Pogg. Ann.*, 1876, **159**, 313; *Ber.*, 1886, **19**, 3187), Rebbs (*Ber.*, 1888, **21**, 596) (both of whom regard the β-form as a hydrate), Oddo (*Gazzetta*, 1901, **31**, ii, 158), and Schenck (*Annalen*, 1901, **316**, 1).

The last-named two authors confirm Marignac's results as to the formation of the β-modification. Schenck, from dilatometer observations at 35°, concluded that a slow reaction, combined with a volume change, takes place in liquid sulphur trioxide, and he assumes the equilibrium $2SO_3 \rightleftarrows (SO_3)_2$.

This view is not confirmed by Lichty's experiments (*J. Amer. Chem. Soc.*, 1912, **34**, 1440).

Now the behaviour of the β-form, more especially as shown by its melting range and the slow rise of vapour pressure, suggested the occurrence of a very slow inner transformation in the solid phase. It was indeed only to be expected in view of (1) the work of H. B. and Mrs. Baker (J., 1912, **101**, 2339) and (2) the self-drying power of sulphur trioxide, that in the distilled material the velocity of inner transformation should be retarded. The present work was accordingly begun early in 1922.

In the meantime, Berthoud (*Helv. Chim. Acta*, 1922, **5**, 4, 513), from observations of the melting points of α- and β-sulphur trioxide and of the vapour pressures of liquid sulphur trioxide, concluded

that only the α-form (m. p. 16·85°) exists. The β-form, showing a large melting range and having an initial melting point dependent on the method of preparation, is regarded as a hydrate, of which he says, "Ce qui est remarquable et tout à fait inattendu, c'est la quantité d'eau extrèmement petite * qui entre dans la composition de cette hydrate et qui suffit pour entrainer un changement profond des propriétés."

Later, Le Blanc and Rühle (*Ber. Mat. phys. Klass. Sächs. Akad. Wiss.*, 1922, **74**, 106) determined the vapour pressures of solid sulphur trioxide phases, obtained by different methods, and of liquid phases up to 20°. They also observed the melting temperatures, and as a result they concluded that sulphur trioxide is a "chemical chameleon." "Wir können nahezu sagen dass wir zwischen 0° und 20° bei jeder Temperatur beliebige Drucke zwischen 20 und 195 mm. erhalten konnten."

Nevertheless, from their chaos of measurements, they think it possible to separate four groups, A, B, C, and D (A having the smallest and D the highest vapour pressures), each corresponding with a definite modification.

The modifications are given as

A, end melting point 95° or 110°;
B, melting point 31°;
C, melting point 16·8°;
whilst D is considered to melt lower than C.

It is to be noticed that only form C, corresponding to the α-form of Berthoud, was readily obtained and that, although the vapour pressures varied too much to allow the vapour-pressure lines to be drawn, great differences were observed between the vapour pressures of the several artificially prepared solid states. Also the vapour tensions of the form D were higher than those of the undercooled liquid.

Le Blanc and Rühle found that the liquid, condensed at 0°, gave varying vapour pressures, and therefore they concluded: "Der Zustand der Flüssigkeit ist bei gleicher Temperatur bei der verschiedenen Versuchen augenscheinlich nicht identisch."

Clearly, then, sulphur trioxide is capable of showing remarkable complexity. Its behaviour as a complex solid was to be expected, since according to our view distillation and drying over phosphorus pentoxide would lead to the formation of a very dry sample in which the velocity of inner transformation would be so slow that the single substance would behave as a mixture.

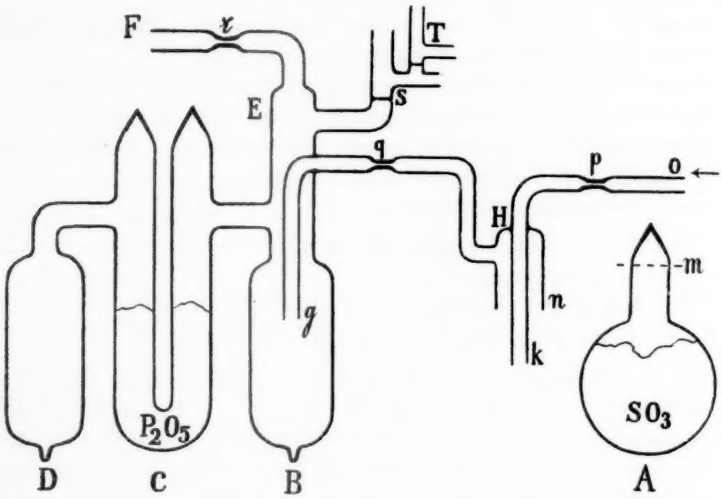
* Estimated at less than 1 molecule per million molecules of sulphur trioxide.

## Experimental.

The apparatus of Jena glass which was used to prepare intensely dried, pure sulphur trioxide is shown in Fig. 1. Two tubes, B and D, are sealed to a U-tube, C. Tube B contains an inner tube, g, which leads to the tube Hn, surrounding a tube, ko. The upper part of tube B ends on one side in a tube, F, leading to a mercury diffusion pump, and on the other side in a T-piece with septum, S.

The method used to fill this apparatus with sulphur trioxide was as follows. While air, dried consecutively by strong sulphuric acid and phosphorus pentoxide, was passing through the tube ok,

Fig. 1.



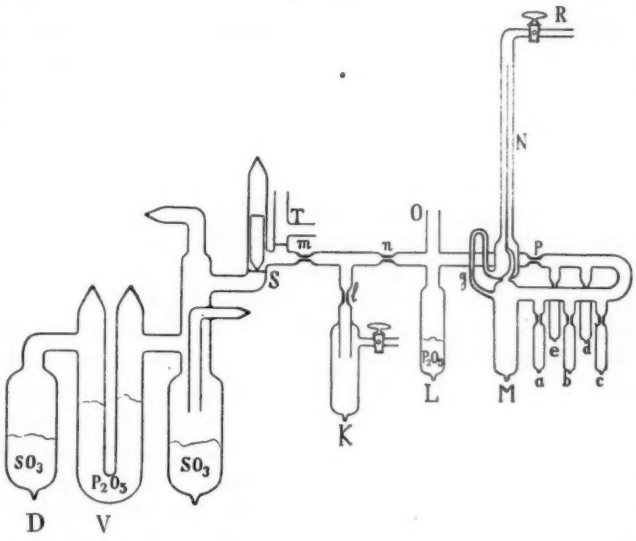

the neck of a cooled bulb, A, containing pure sulphur trioxide (Kahlbaum), was cut off at m and immediately sealed to the tube Hn. The U-tube, C, was now filled with pure phosphorus pentoxide and the ends were sealed off while dry air was circulating through the apparatus. The tube ok was sealed at p, a U-tube cooled in liquid air was placed between F and the pump, the bulb A was cooled in a mixture of alcohol and solid carbon dioxide, and the apparatus was evacuated and sealed off at r. The sulphur trioxide was then distilled from A into B, and q was sealed off.

When the drying apparatus had been filled in this way, we applied forced drying by distilling the sulphur trioxide from B to D and then from D to B, one vessel being cooled in solid carbon dioxide and alcohol while the other remained at room temperature. This drying process was repeated every day for a month or longer.

A breaker of solid glass was now carefully placed on the septum S, and after a second T-piece with septum had been sealed to the delivery tube our storing apparatus was ready.

The apparatus for determining the vapour pressure is shown in the right half of Fig. 2. MN is a glass spring indicator * with the bulb, M, and the mantle, N, still in connexion through the capillary, g. The bulb, M, is connected to a wide horizontal U-tube, to which five vertical small tubes with capillaries, a, b, c, d, and e, are sealed. The further connexions with the vessels L and K and with the storing apparatus are evident from Fig. 2.

FIG. 2.




Before the apparatus is charged with sulphur trioxide, phosphorus pentoxide should be distilled into vessel L. Tube O was therefore sealed to an apparatus so that pure phosphorus pentoxide could be distilled in a current of intensely dried air. Previous to this, the apparatus was heated in a current of dry air, driven through every tube and vessel. The capillary ends of these tubes and vessels were then sealed off successively.

When pure phosphorus pentoxide had been distilled into vessel L, tube O was sealed off and tube R connected to the mercury diffusion pump. After the apparatus had been heated with a large Teclu

* This pressure indicator is based on Jackson's principle (J., 1911, 99, 1066).

burner and evacuated until a high vacuum was reached ($10^{-6}$ mm. Hg), connexion between the mantle of the glass spring and the vessel M was broken by sealing off the capillary tube, g.

The bulb, D, containing the sulphur trioxide was now cooled in a mixture of alcohol and solid carbon dioxide and the septum S was broken by shaking the apparatus. The apparatus was again connected to the high vacuum pump, but now by the delivery tube of vessel K, and, while this vessel was cooled in liquid air and the cock of the delivery tube was open, a portion of the sulphur trioxide was distilled into K,* the temperature of the vessel D being allowed to rise from $-80°$ to $+18°$. After that, D was again cooled to $-80°$ and the capillary l sealed off. Now vessel L, containing phosphorus pentoxide, was cooled to $-80°$ while the temperature of vessel D containing sulphur trioxide rose to 18°. When sufficient sulphur trioxide had been distilled into L, the capillary at n was sealed off. As indicated in Fig. 2, it was possible to distil the sulphur trioxide from L into M and then to seal off the capillary, p. As a rule, however, L and M were left in connexion with one another.

The apparatus was now set up rigidly, L cooled in liquid air, and R connected to a high vacuum pump in order to fix the zero position of the needle of the glass spring by means of two strips of paper, on which were drawn very fine straight lines. One strip was stuck to the back and the other to the front so that the line on the back strip, the point of the needle, and the line on the front strip were in alignment. The whole apparatus was placed in a thermostat and tube R was connected to a mercury manometer containing two T-pieces with cocks, so that, when required, the pressure could be changed until the needle of the glass spring was in the zero position. In this case, the pressure inside the glass spring, and consequently inside the apparatus, was equal to the pressure indicated by the mercury manometer. This was the method of measuring the vapour pressures.

The sample of sulphur trioxide obtained in this way was an ice form and above 18° was a clear liquid without a trace of a solid form. By cooling in liquid air or distilling repeatedly from 18° to $-80°$, the asbestos form could always be obtained, but so long as the other, more volatile, ice form was present, the pressure was that of the latter.

The sulphur trioxide obtained by the method described here was found to be very pure; it contained at the most only a trace of sulphur dioxide (less than 0·1%).

* By this means we obtained in K a solid distillate with an initial melting point of 80°. After resolidification, the melting point was 32°.

*The Ice Form.*

*Determination of the Vapour Pressure of the Intensively Dried Substance.*—Our first determinations of the vapour pressure are given in Table I.

TABLE I.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0° | 207·8 | |
| 6·4 | 226·8 | |
| 11·7 | 254·7 | Melting begins between these temperatures. |
| 14·7 | 215·8 | |
| 16·95 | 168·9 | $SO_3$ for the greatest part molten, except for some crystals of a higher-melting form. |

We see here that melting takes place over a temperature range and that during the melting process the pressure is sinking. After the apparatus had stood for 18 hours at 18°, the temperature of the thermostat was lowered and the former experiment repeated with the following results.

TABLE II.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 1·4° | 149·6 | |
| 7·9 | 188·4 | |
| 11·6 | 224·3 | Melting begins. |
| 15 | 207·4 | |
| 16·34 | 175·6 | |
| 19·1 | 188·6 | All molten except some crystals of a higher-melting form. |
| 22·33 | 229·5 | |
| 25·12 | 271·4 | |
| 27·97 | 319·2 | |
| 32·28 | 406·9 | |

Thus, after 18 hours, the vapour pressure had fallen, and this induced us to maintain the apparatus for a further 40 hours at 18°, to see whether the pressure would sink still more. After that period, the determination of the vapour pressures gave the following results.

TABLE III.

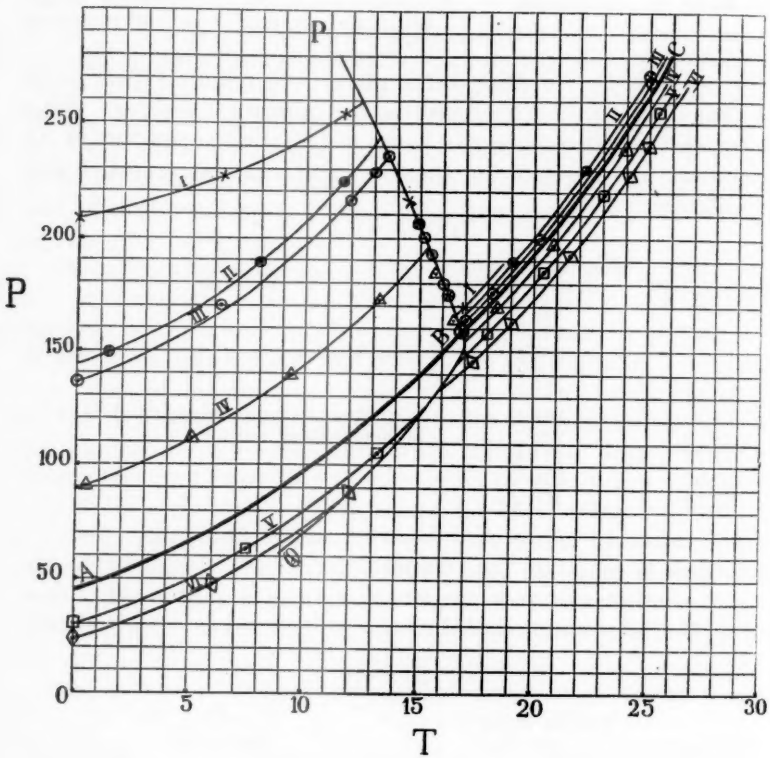
| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0·35° | 136·4 | |
| 6·28 | 170·2 | |
| 12·05 | 215·8 | |
| 13·01 | 227·8 | |
| 13·62 | 236·8 | Melting begins. |
| 14·6 | 215·8 | |
| 15·1 | 200·9 | |
| 15·5 | 192·9 | |
| 16·0 | 180·0 | |
| 16·95 | 165·0 | All molten except some crystals of a higher-melting point. |
| 18·2 | 175 | |
| 20·3 | 200 | |
| 25·1 | 266·7 | |

Plotting the vapour pressures recorded in these three tables as a function of the temperature, we get the $P$–$T$ diagram (Fig. 3).

The results of our first series of experiments are indicated by $\times$, the results of the second by $\otimes$, and the results of the third by $\odot$.

It is clear that the vapour pressure of the solid phase diminishes markedly with time, for instance, at 0° from 207·8 mm. to 136·4 mm.

FIG. 3.




of mercury. It is further remarkable that, when melting has begun and the pressure is sinking, the vapour pressures measured during this melting process lie on the same curve, the vapour pressure line of the three-phase equilibrium solid–liquid–vapour.

As the vapour pressure of the solid phase was much lower after each period of rest at 18°, the vapour pressure lines of the liquid phase were also sinking, but the difference in this case was only small.

Consequently, the result was that for every new series of determinations a lower curve was found for the equilibrium solid–vapour, the same curve for the equilibrium solid–liquid–vapour, and a slightly lower curve for the equilibrium liquid–vapour.

Further, the fall in the vapour pressure was rather rapid at the beginning, when the pressure was high, but the decrease became much slower after 40 hours. To get a still larger fall, it would be necessary to wait a very long time.

As will be clearly demonstrated later, the above results prove that sulphur trioxide is composed of molecules of different kinds and that when sulphur trioxide is dried intensively, the inner transformations between these different molecular species are very slow. Similar facts have already been established in the case of violet phosphorus, where it was found possible to obtain a continuous fall of the vapour pressure of the remaining phosphorus by distilling off a portion at a relatively low temperature ("The Theory of Allotropy," p. 215). The success of the method in that case led to its adoption in the present work.

Therefore, after having condensed the sulphur trioxide in M, we distilled a portion by cooling tube e in a bath of solid carbon dioxide and alcohol. Although the remainder of the apparatus, including M, was at room temperature, the sulphur trioxide in M became solid owing to the cooling caused by evaporation.

After sealing off the tube e, the vapour pressures were redetermined, with the following results.

TABLE IV.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0·53° | 90·7 | |
| 5·2 | 112·7 | |
| 9·46 | 139·8 | |
| 13·3 | 172·6 | |
| 15·55 | 184·1 | Melting has begun. |
| 16·4 | 162·8 | |
| 18·4 | 169·6 | All molten except the crystals of a higher-melting form. |
| 20·94 | 197·4 | |
| 24 | 238·9 | |

Thus, as in the case of violet phosphorus, the vapour pressure of the solid phase (see curve IV) is distinctly reduced by partial evaporation.

The method of distillation here proved to be very effective. We continued to apply it in order to get phases with still lower vapour pressures, and accordingly distilled a portion into tube d, which was then sealed off. The vapour pressure had again fallen, as shown in the following table.

TABLE V.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0° | 30·2 | |
| 7·5 | 63·0 | |
| 13·2 | 105·1 | |
| (15·3 | 124·0) | Melting begins. |
| (16·6 | 144·5) | End of melting range; all molten except the crystals of a higher-melting form. |
| 18 | 157·3 | |
| 20·5 | 184·3 | |
| 23·1 | 218·9 | |
| 25·4 | 253·6 | |

The corresponding curves, marked V in Fig. 3, are in a very remarkable position. The vapour-pressure line of the solid phase, which previously was above that of the liquid, now lies below it, so that we have realised a part of the three-phase line S–L–G, in which the pressure increases with rise in temperature. Further, the initial melting point has fallen.

Having obtained this very interesting result, we again distilled a part of the sulphur trioxide into tube c, after which this tube was sealed off. The residue now showed the following vapour pressures.

TABLE VI.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0·4° | 24·4 | |
| 6·1 | 47·6 | |
| (11·6 | 84·0) | Melting begins. |
| 12·1 | 86·2 | |
| (15·9 | 133·0) | End of melting range. |
| 17·4 | 145·1 | |
| 18 | 150·7 | |
| 19·1 | 162·5 | |
| 19·7 | 169·1 | |
| 21·6 | 192·3 | |
| 24·2 | 228·2 | |
| 25 | 240·1 | |
| 28·5 | 310·0 | |

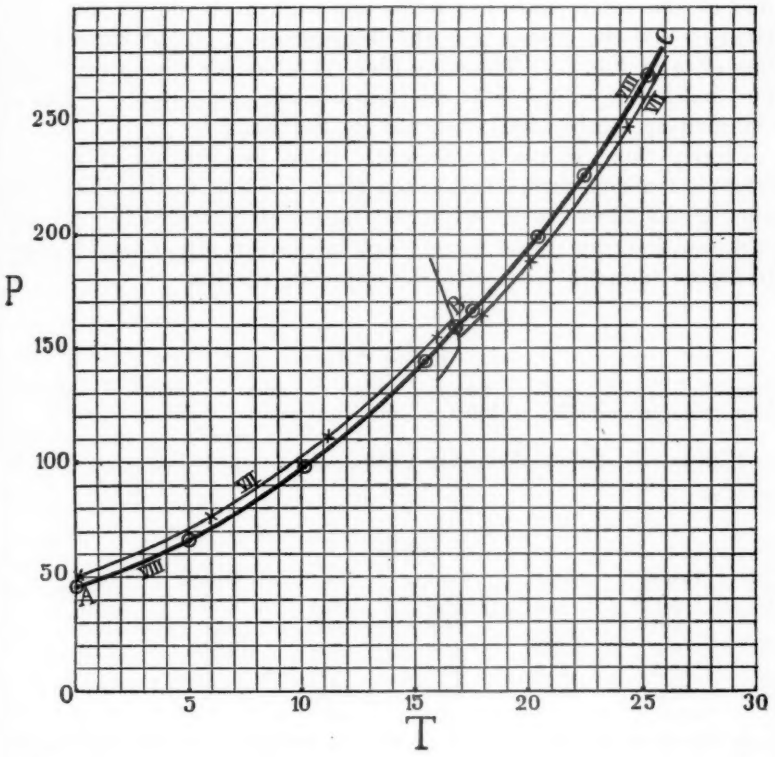
These results, indicated by VI in Fig. 3, show that the effect of the former distillation is now still more pronounced. The vapour pressure has fallen again and melting takes place over a range of about 4°.

*Vapour Pressure of the Insufficiently Dried Substance.*—Another remarkable result was obtained with a sample of sulphur trioxide which had been dried for only a few days instead of a month. In this case, we obtained directly a preparation of rather low vapour pressure, as is seen from the following table.

TABLE VII.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0·15° | 48·8 | |
| 5·95 | 75·7 | |
| 11·2 | 112·4 | |
| 16·02 | 155·1 | |
| 18 | 164·5 | |
| 20·1 | 188·5 | All molten except some of the higher-melting form. |
| 24·4 | 246·5 | |

FIG. 4.




The vapour-pressure line of the solid phase is a little above that of the liquid phase. After 120 hours, the vapour pressure was again determined. Throughout this series of observations the temperature was allowed to increase only very slowly, and before a determination was made the apparatus was maintained at constant temperature for a long period to ensure complete inner equilibrium.

The results recorded in Tables VII and VIII are plotted in Fig. 4.

TABLE VIII.

| Temperature. | Vapour pressure in mm. Hg. | Remarks. |
|---|---|---|
| 0·15° | 45·5 | |
| 5·0 | 66·0 | |
| 10·2 | 98·2 | |
| 15·5 | 144·4 | |
| 17·6 | 166·4 | |
| 20·5 | 198·5 | All molten except some crystals of a higher-melting form. |
| 22·5 | 225·9 | |
| 25·3 | 270·4 | |

The effect of standing for 120 hours is that the vapour-pressure line of the solid phase has fallen and that of the liquid phase has risen to just the extent that the lines intersect on the three-phase line (P Q in Fig. 3). Therefore there is no longer a melting range, but melting is complete at one temperature, *viz.*, 16·8°.* This is the melting temperature observed by Berthoud.

Clearly then, in the insufficiently dried preparation of sulphur trioxide transformation had taken place, leading to the disappearance of the effects of complexity. Later, we extended the vapour-pressure determinations for the not intensively dried liquid phase to higher temperatures, with the following results.

TABLE IX.

| Temp. | 30·65° | 35·0° | 40·5° | 45·0° | 49·75° |
|---|---|---|---|---|---|
| Vap. press. in mm. Hg. | 359·3 | 460·7 | 608·9 | 777·2 | 977·2 |

Taking the values of Tables VIII and IX and calculating $T \ln P$, we get

TABLE X.

| Temp. | $T \ln P$. | Temp. | $T \ln P$. | Temp. | $T \ln P$. |
|---|---|---|---|---|---|
| 0·15° | 104·3 | 20·5° | 1553 | 40·5° | 2010 |
| 5·0 | 1164 | 22·5 | 1602 | 45·0 | 2116 |
| 10·2 | 1299 | 25·3 | 1658 | 49·75 | 2222 |
| 15·5 | 1434 | 30·65 | 1786 | | |
| 17·6 | 1486 | 35·0 | 1889 | | |

If $T \ln P$ is plotted against $T$ (Fig. 5), the points lie exactly on two straight lines, proving that the heats of evaporation of the solid and liquid phases for this temperature range are not functions of the temperature.

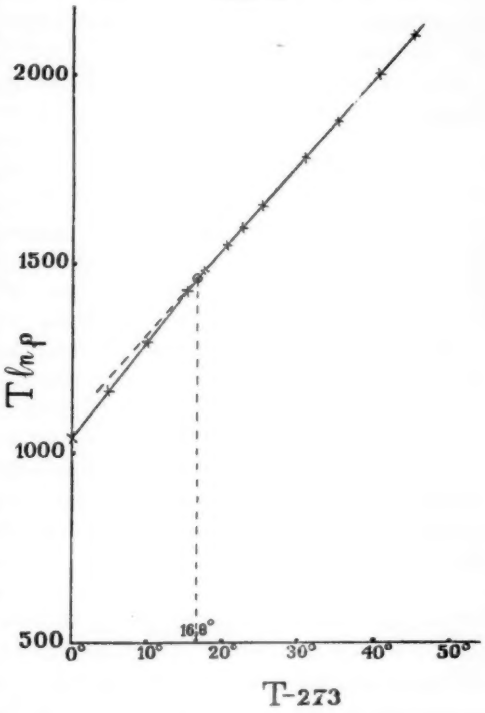
* In another case also, we observed complete melting at the same temperature, as by mere chance, after a dry preparation had been evaporated, the vapour-pressure line of the solid phase intersected the three-phase line just at the point where the temperature is a maximum. This is in agreement with the theory of three-phase lines.

As already indicated in the tables, there were nearly always at least two forms of sulphur trioxide, the ice form and the asbestos form, side by side in our apparatus. This also occurred in the last experiments, but, as may be seen from the results, the presence of the solid asbestos form did not prevent the determination of the vapour-pressure lines of the solid and liquid phases of the ice form, whether it behaves as a mixture or as a real single substance.

Le Blanc and Rühle also found the vapour pressure of the ice form to be independent of the presence of the asbestos form, and this, as will be seen later, is in complete agreement with the theory.

The fact that all the vapour-pressure lines of the solid phase end in points on the same three-phase line P Q (see Fig. 3) proves that all these lines relate to the *same* crystal form of sulphur trioxide, *viz.*, the ice form.

FIG. 5.




*Discussion of Results.*

We have found that after the ice form of sulphur trioxide had stood for 56 hours at 18° the vapour pressure at 0° diminished by 71·4 mm. of mercury, and that by distillation of this preparation the vapour pressure could be changed continuously until a residue with a vapour pressure at 0° of 22 mm. of mercury was obtained, the initial value having been 207·8 mm. Whilst the vapour pressure diminished, the initial melting point first rose and then fell.

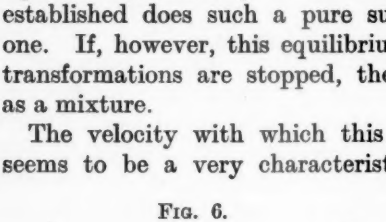
All these different solid phases belong to the ice form, since they gave melting ranges which fell on the continuous three-phase line corresponding to the equilibrium solid–liquid–vapour for a dissociable compound.

The old considerations of the different states of aggregation

cannot give an explanation of these facts. The theory of allotropy, however, offers no difficulty at all. On the contrary, these results are valuable confirmation of this theory, because it assumes that every state of aggregation of a simple substance is complex, every crystalline state consisting of mixed crystals, built up from molecules of different kinds. These different kinds of molecules can change into one another; the transformation can lead to a chemical equilibrium, and only when this equilibrium (inner equilibrium) is established does such a pure substance behave as a real single one. If, however, this equilibrium is established slowly, or if the transformations are stopped, then a pure substance will behave as a mixture.

The velocity with which this inner equilibrium is established seems to be a very characteristic property of a substance; so that there are "rapid" substances and "slow" substances. Rapid substances can undergo rapid changes, being always in a state of inner equilibrium, but slow ones cannot. In the light of these considerations the results obtained here can be easily explained. We assume that the system sulphur trioxide is composed of at least two different kinds of molecules, α and β, which molecules can not only change one into the other, but can also give a dissociable compound, αβ. These transformations can lead to an inner equilibrium indicated as

FIG. 6.




$$\left.\begin{matrix}\alpha \\ \downarrow\uparrow \\ \beta\end{matrix}\right\} \rightleftarrows \alpha\beta.$$

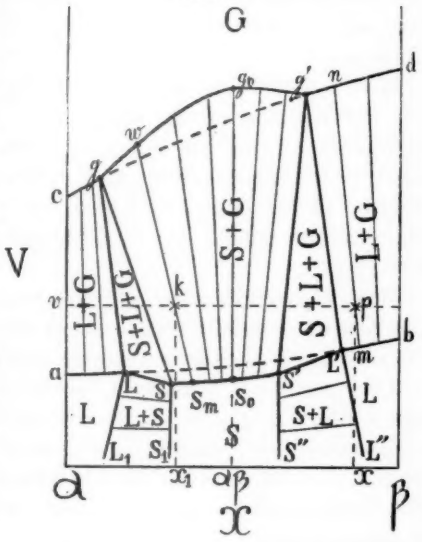
Our experiments show that sulphur trioxide is a slow substance, consequently the inner equilibrium is being established slowly, even before intensive drying, whilst after intensive drying it is being established with extreme slowness or not at all.

At this point, it should be remembered that, as shown by van der Waals, the three-phase line, P Q, of a dissociating compound, composed of a volatile component α and a less volatile component β, has the form given in Fig. 6 and that if the compound can exist with a vapour of the same composition, there is a sublimation curve at f′ tangential to the three-phase line P Q at the maximum sublimation point f′, just as the melting line of the compound is tangential at f, the minimum melting point. The result is that

the dissociating compound does not exhibit a single melting point when subject to its own vapour pressure, but rather a melting range, f to f′. In other words, with the pure compound we can realise a small portion of the three-phase line P Q. We see from the form of the three-phase line that at every temperature, except the maximum temperature, there can exist two three-phase equilibria with different vapour pressures. These will be mentioned later.

One has also to consider which co-existence can be realised here with a mixture of definite composition, especially if the volume of the vessel is relatively large. This can only be done by using, as van der Waals did, the $V$–$x$ diagram, in which the molecular volume $V$ is plotted against the composition $x$, expressed as molecular per cent. The only change necessary here in the $V$–$x$ diagram of van der Waals involves the mixed crystal phases.

Fig. 7.




As a simplification, we will assume that at the temperature considered, the compound alone appears in the solid state, the forms α and β being liquid. The $V$–$x$ diagram is then given by Fig. 7. At this temperature, a is the molecular volume of liquid α under its own vapour pressure, and c is the molecular volume of gaseous α at the same vapour pressure, in equilibrium with the liquid phase. The points b and d have the same significance with respect to the component β. The line ab, the binodal for the liquids, gives the molecular volumes of the liquid mixtures, whilst cd, the binodal for the vapours, gives the molecular volumes of the gaseous mixtures. Consequently in this diagram every phase is indicated by its $V$ and $x$ values, and corresponding points on the lines ab and cd represent phases in equilibrium. A line can be drawn from any point on the line ab (representing any given liquid phase) to a point on the line cd, representing the vapour phase in heterogeneous equilibrium with the liquid. These lines are termed nodal lines. If α is more volatile than β, the vapour will, in general, be richer in the α component, so that the nodal lines

starting from line ab will run to the left, except in the case of pure $\alpha$ or $\beta$, when they run vertically.

Consider a point p, representing a composition $x$ and a volume $v$, situated in the region between the liquid and vapour binodals. The compositions and volumes of the two co-existing phases are given by the co-ordinates of the points m (liquid) and n (vapour); mn being the nodal line through p. The quantities of the phases "m" and "n," which together form the system "p" are, of course, in the ratio np/mp.

Now a portion of the possible equilibrium, liquid–vapour, is metastable, because the compound $\alpha\beta$ has been assumed solid at the temperature considered. Corresponding with this stable state, the solid compound will appear in the central part of the $V$–$x$ diagram.

If a vertical line is drawn through the point corresponding to the composition of the compound, $S_0$ on this line represents the molecular volume of the solid, which is lower than that of the supercooled liquid compound, whilst $g_0$ represents the molecular volume of the co-existing gas phase, which is higher than that of the vapour phase in equilibrium with the supercooled liquid compound.

Now the equilibrium of two phases in a system of two components at constant temperature is univariant and thus there will be a series of equilibria between solid and vapour phases.

This series of equilibria, solid–vapour, is represented by the space $S S_0 S' g' g_0 g$ in the $V$–$x$ diagram. The line $S S_0 S'$ gives the compositions and molecular volumes of mixed crystals of the compound $\alpha\beta$ with either of its components $\alpha$ or $\beta$, the line $g g_0 g'$ giving the compositions and molecular volumes of the corresponding vapour phases.

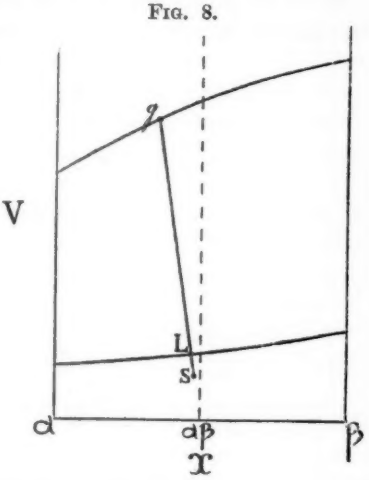
This region of equilibria between mixed crystals and vapour will end abruptly on both sides at the lines S g and S′ g′, respectively, since here we enter into regions of three-phase equilibria S–L–G; it will be seen that the vapour line of the system mixed crystal–vapour intersects the vapour lines of the systems liquid–vapour at g and g′. Thus we get the triangles S G L and S′ G′ L′, marking the regions of three-phase equilibria. Every point in these triangles represents a three-phase system in equilibrium and from the position of the point the quantities of the three phases can easily be deduced.

Passing now to higher temperatures, the liquid line ab rises a little just as the solid line S S′, whilst the vapour lines cd and $gg_0g'$ sink. Most interest, however, attaches to the movements of the nodal lines g L and g′ L′. With rising temperature, these lines obviously move towards the centre, and,

as van der Waals showed, the movement of g′ L′ is such that it passes through the line of the compound ($g_0$ $S_0$). First, at the maximum sublimation temperature, g′ lies on the line of the compound (at $g_0$) and subsequently, at the minimum melting temperature, L′ lies on this line (at $S_0$). Finally, the points g and g′, and L and L′ coincide and the two three-phase triangles reduce to one straight line (see Fig. 8) which gives the highest three-phase equilibrium in relation to the temperature.

As apparent from Fig. 6, there are, at any temperature below the maximum three-phase temperature, two three-phase equilibria of different compositions; for the equilibrium with the higher vapour pressure, the composition must correspond to a point in the triangle S g L (Fig. 7), and for the system with the lower vapour pressure, the composition must correspond to a point in the triangle S′ g′ L′.

Fig. 8.




Further, if we have in our vessel of volume $v$ a mixture of the composition $x_1$, the state is indicated by the point k. This point does not lie in a three-phase domain but in a two-phase domain (mixed crystals–vapour). From the nodal line passing through this point k we can deduce the quantities of the two co-existing phases, namely, wk/w$S_m$ gram-mols. of the mixed crystal phase of composition Sm, and $S_m$k/w$S_m$ gram-mols. of vapour of composition $w$.

As mentioned above, it appears that at higher temperatures the nodal line g S moves to the right. Consequently, at a definite temperature the point k will enter the shifted triangle S L g, which signifies that from the two-phase equilibrium, mixed crystals–vapour, we get a three-phase equilibrium, mixed crystal–liquid–vapour. As long as point k lies in this three-phase triangle we naturally realise points on the three-phase line P Q in the *P–T* diagram. When, by movement of the three-phase triangle with rising temperature, the point k passes the line g L, the solid phase disappears and we get the two-phase equilibrium liquid–vapour.

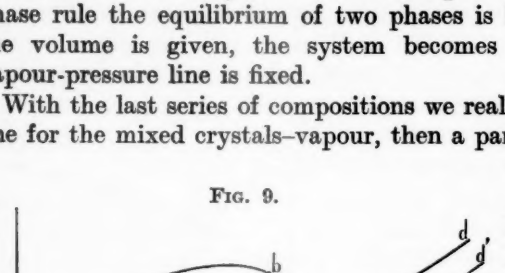
If the composition had lain more to the right, nearer to that of the compound, the point k would have entered the other three-phase triangle S′ L′ g′ and we should have realised points on the lower part of the three-phase line P Q in the *P–T* diagram, until

the point k passed the line L′ g′, when there would be obtained again a two-phase equilibrium, liquid–vapour. Changing the composition from left to right in different experiments, for instance, by distillation of the mixed crystal phase so that it becomes poorer in the more volatile component α, we realise with our first series of compositions a vapour-pressure line for the mixed crystals–vapour, then a portion of the upper three-phase line, and finally a vapour-pressure line for liquid–vapour.

Since we have a system of two components, according to the phase rule the equilibrium of two phases is bivariant, so that, if the volume is given, the system becomes univariant and the vapour-pressure line is fixed.

With the last series of compositions we realise a vapour-pressure line for the mixed crystals–vapour, then a part of the lower three-phase line, and finally a vapour-pressure line for the system liquid–vapour.

FIG. 9.




A singular case arises when the point k lies on the line, which is the limiting case of the two three-phase triangles at the maximum temperature of three-phase formation. In this case we cannot realise a portion of the three-phase line P Q, but only one point, consequently melting takes place at one temperature just as with a single substance. In a system of two components a three-phase system is univariant, but at the maximum three-phase temperature we have the extraordinary circumstance that the change in volume with transformation of solid and vapour to liquid is zero and thus the three-phase system becomes invariant at this point.

Finally, if the compound has a sublimation line, this line is the lowest curve for the equilibrium mixed crystal–vapour, and consequently forms the limit attainable by distillation of the mixed crystals. As mentioned above with reference to Fig. 6, the sublimation curve lies below the lower branch of the three-phase line and touches this line at the maximum sublimation point.

We will now indicate in a *P–T* diagram what has been discussed regarding the vapour-pressure lines of mixtures obtained by distillation of the mixed crystal phase of the compound αβ. Drawing,

then, the vapour-pressure lines (1) of a mixture richer in α than the compound αβ, and (2) of the mixture after distillation, which possesses a composition a little poorer in α than the compound αβ, we get Fig. 9.

The *P–T* lines of the original mixtures are given as ab, bc, and cd, and those of the residues after distillation as a′b′, b′c′, and c′d′. Between these two extremes there are naturally other mixtures giving lines in intermediate positions. Passing from the vapour-pressure lines of the original mixture, that is, the lines ab, bc, and cd, to lines for mixtures containing less and less of the α component, the portion of the three-phase line corresponding to bc will shrink until b and c coincide. This coincidence occurs when the temperature of liquefaction is a maximum. Passing this composition, we should find that the point b has passed c and the intercept on the three-phase line would increase.

In the limiting case, b′ will have reached the maximum sublimation point and the line a′ b′ will have fallen below the three-phase line, with the exception at the maximum sublimation point where the two lines touch one another.

The foregoing theoretical considerations regarding the three-phase lines of a dissociable compound enable us to interpret the experimental results obtained with the ice form of sulphur trioxide (Fig. 3). It is clear that dried sulphur trioxide behaves exactly as a mixture of a system of two components which give a dissociable compound, the initial composition of the mixture lying towards the side of the more volatile component.

We have proved that even the most intensively dried solid preparation gives a slow decrease in the vapour pressure if this pressure is relatively high, and a slow increase if the vapour pressure is very low. This behaviour shows that reactions leading to the attainment of inner equilibrium are taking place even in the case of the dried solid phases. With insufficiently dried preparations, these reactions were much faster, so that after 120 hours the behaviour as a mixture had disappeared and the ice form behaved as a real single substance should.

In this case the inner equilibrium

$$\left.\begin{matrix}\alpha\\ \uparrow\downarrow\\ \beta\end{matrix}\right\} \rightleftharpoons \alpha\beta$$

must have been established and our experiments show that, in this case, when sulphur trioxide behaves as a unary system, the vapour-pressure lines meet the three-phase line in a point above the minimum melting point of the compound, even above the temperature maximum, from which it follows that at equilibrium

the ice form contains more of the α constituent than corresponds with the composition of the compound. It appears, further, that the substance described by Le Blanc and Rühle as the D-modification (see above) must be a mixture which is a little richer in the α-pseudo-component than the ice modification.

We have treated in this communication only the ice-form modification of sulphur trioxide and studied the region of the pseudo-system in which the ice form is situated. This is the region of a dissociable compound of pseudo-components, which are related as polymerides or isomerides, using these terms in the widest possible sense.*

The ice form of sulphur trioxide is one of the two metastable modifications. The other part of the system, however, in which the second metastable modification and the stable modification are situated, is not less interesting.

The other metastable form is the one which often makes up three-quarters of the sulphur trioxide in the bulbs delivered by Kahlbaum. The appearance is asbestos-like and we will speak of it as the "low-melting" asbestos form. This modification has already been studied and, if not intensively dried, exhibits a unary behaviour, with a triple point at 32·5° and 31 cm. of mercury.

The stable modification of sulphur trioxide, which we will call the high-melting asbestos form, exhibits more strongly than any other the property of decreasing its vapour pressure on distillation of the intensively dried preparation. We can further study this form at higher temperatures and the reversal to the earlier state is thus more marked. By distillation at 60°, a solid residue of abnormally low vapour pressure (59 cm. of mercury) was obtained; after 13 hours at this temperature, however, the vapour pressure had increased to 94 cm. Even this rise of 35 cm. is not the largest possible. Since we can clearly get different states of this high-melting asbestos form with very different vapour pressures, it is to be expected that widely different initial melting points will be obtained. Melting points differing 10°, 20° or more have been observed. Details of the investigation of the high-melting asbestos form will appear in a subsequent paper, and it need only be stated here that the results agree with those obtained in the study of violet phosphorus.

* The new ideas on atomic structure show that fine differences are possible between atoms of the same element. These differences are, for instance, connected with a change in the quantum numbers of the valence electron orbits, and such different atoms can give rise to molecules with finer differences than are commonly exhibited by isomerides. It is clear, however, that in a broad conception of the idea "isomerism," this term will include these different molecular species.

Some have thought that, possibly, varying size of grain might account for the difference in vapour pressure. Meissner (*Z. anorg. Chem.*, 1920, **110**, 169), however, has shown that such influences are extremely small and cannot explain the phenomena observed, for instance, with violet phosphorus, when changes in vapour pressure of 2 atmospheres were recorded.

We thus see that the behaviour of sulphur trioxide furnishes another convincing confirmation of the theory of allotropy.

*Summary.*

In view of the strong self-drying power of sulphur trioxide it was expected that after distillation and subsequent drying over phosphorus pentoxide the residue would be so dry that the attainment of inner equilibrium would be sufficiently slow for the single substance to behave as a mixture. This has been realised experimentally.

It has not only been proved that the intensely dry solid and liquid states behave as mixtures, but the continuous change in the vapour pressure of the solid (ice-form) phase, caused by distillation, enabled the domain of the pseudo-system to which the ice form belongs, to be studied. It is the domain of a dissociable compound, which, if behaving as a unary system (*i.e.*, as one component), consists of mixed crystals in inner equilibrium with a composition a little richer in the more volatile pseudo-component than the compound.

In addition to the changes in the vapour pressure of the solid phase, corresponding changes in the melting ranges have been observed.

Similar phenomena have been observed in the study of the two asbestos forms and will be communicated in detail in a later paper.

THE UNIVERSITY, AMSTERDAM. [*Received, July 9th*, 1924.]

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# CCCLII.—*The Complexity of the Solid State. Part II. The Behaviour of Phosphorus Pentoxide. Part I.*

By ANDREAS SMITS and AREND JOAN RUTGERS.

## *Introduction.*

THE experiments of H. B. and Mrs. Baker (J., 1912, **101**, 2339; 1922, **121**, 568) showing the enormous drying power of phosphorus pentoxide and the resulting changes in properties of substances when dried by this compound, are of great importance to the theory of allotropy. Now it might be expected that the pentoxide would have a great self-drying power and that distillation

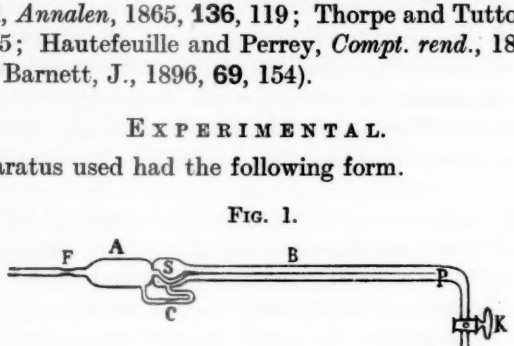
of the pentoxide itself would yield a more intensely dried material than any we now know. Since other substances, if intensively dried, exhibit their complexity (see preceding paper), it was anticipated that the study of the oxide, prepared in this manner, would give particularly interesting results (see this vol., p. 1068).

Among the few statements about phosphorus pentoxide found in the literature are that it sublimes at 250° and that, at 440°, the volatile, crystalline modification is transformed into a less volatile, amorphous form which, at red heat, passes into a glass (Grabowski, *Annalen*, 1865, **136**, 119; Thorpe and Tutton, J., 1890, **57**, 369, 545; Hautefeuille and Perrey, *Compt. rend.*, 1889, **99**, 33; Tilden and Barnett, J., 1896, **69**, 154).

## Experimental.

The apparatus used had the following form.

Fig. 1.




A bulb, A, ending in a spring, S, and a needle pointer, P, is sealed to a mantle, B, drawn out into a tube, D, which carries a stop-cock, K.* The bulb A and the mantle B are connected by a capillary tube, C. After the apparatus, made of high-melting Jena glass (in some experiments quartz was employed), had been steamed and dried, tube F was sealed to the phosphorus pentoxide distilling tube (see this vol., p. 1068) whilst tube D was connected by a short rubber tube with a U-tube filled with phosphorus pentoxide and then with a wash-bottle containing strong sulphuric acid.

The apparatus was heated to redness whilst carefully dried air was passing through the distilling tube. On distilling the phosphorus pentoxide, the sublimed oxide was deposited in the end of the distilling tube, from which it was distilled into A by further heating. The pentoxide so obtained was an exceedingly fine, crystalline substance. The capillary at F was then sealed off and the apparatus evacuated by a mercury diffusion pump connected to D. When a vacuum of about $10^{-5}$ mm. of mercury was reached, the capillary C was sealed, thus cutting off tube A from the mantle tube B. The apparatus was now placed vertically in a hole (22 cm. deep and 25 mm. wide) in a large cylindrical iron block packed

* This pressure indicator is based on Jackson's principle (J., 1911, **99**, 1066).

with a layer of asbestos (6 mm. thick) round which a nickel-chromium wire was wound, the whole being finally insulated by a layer of asbestos 10 cm. thick.

The zero position of the needle point of the spring had now to be fixed, and since the vapour pressure of phosphorus pentoxide is zero at the ordinary temperature, the adjustment was readily performed at this temperature by the method described in the preceding paper. The vapour pressures of the oxide could then be determined by the method previously described.

The temperature of the bulb A during an experiment was obtained with a calibrated thermo-element placed close to it, the whole being thoroughly lagged with asbestos.

The vapour pressure of the fine crystalline sublimate could be determined only up to 400°, since at higher temperatures it was transformed into a modification having a very low vapour pressure. Most remarkable is the fact that the vapour pressures of the preparations varied with the velocity of distillation, which proves that such preparations are not in a state of equilibrium. Provided the preparations were not heated to too high a temperature, they gave the same vapour pressures with rising or with falling temperature. Table I shows that at about 370° the vapour pressures of two preparations are 1·8 and 2·05 atmospheres, respectively.

TABLE I.

| Preparation. | $t°$. | $T°$ abs. | $p$=Pressure in cm. Hg. | $P$=Pressure in atmos. | $T \ln P$ or $2{\cdot}3025\, T \log_{10} P$. |
|---|---|---|---|---|---|
| 1 | 296 | 569 | 10·9 | 0·143 | −1105 |
| | 324 | 597 | 30·4 | 0·400 | − 546·8 |
| | 351 | 624 | 67·5 | 0·884 | − 76·7 |
| | 375 | 648 | 141·4 | 1·865 | 404 |
| | 406 | 679 | 323·7 | 4·259 | 984 |
| 2 | 276 | 549 | 7·2 | 0·095 | −1293 |
| | 304 | 577 | 22·0 | 0·289 | − 716·6 |
| | 315 | 588 | 29·7 | 0·391 | − 552·2 |
| | 361 | 634 | 122·1 | 1·608 | 300·9 |
| | 377 | 650 | 200·0 | 2·631 | 629 |

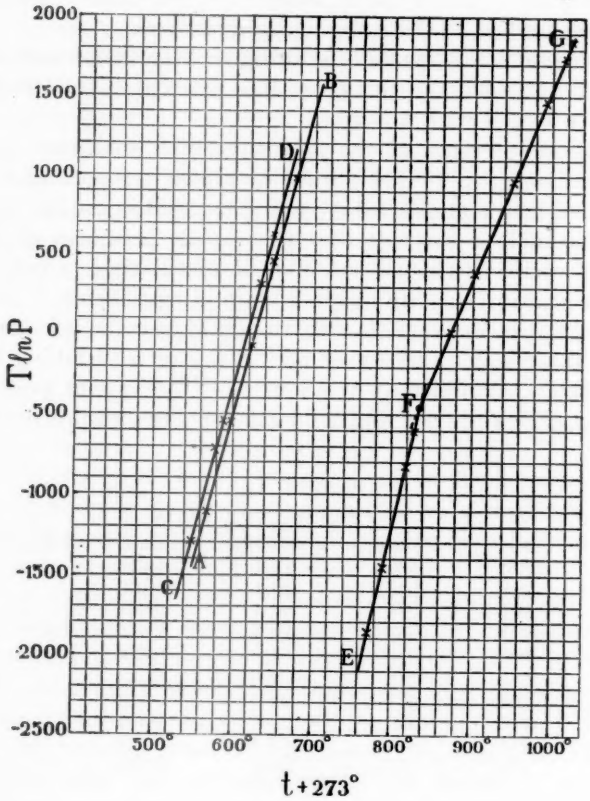
At about 400°, as mentioned above, the very volatile forms, which are metastable, are transformed into a less metastable modification, and the vapour pressure falls continuously to 0·02 cm. of mercury.

An unlimited number of similar vapour-pressure lines can be realised and, just as the initial preparations show differences, so do the transformed modifications, although here the differences are not so large and it is very probable that, after a sufficient time, constant end values would be obtained.

Another remarkable fact, closely connected with the above, is

that, although the phosphorus pentoxide was entirely free from any trace of trioxide and phosphoric acid, the transformed modifications of low vapour pressure melted, not at one temperature, but over a temperature range. This is shown in Table II; the results were obtained with a quartz pressure indicator.

FIG. 2.




Plotting the results given in Tables I and II on a $T \ln P$–$T$ diagram, we obtain Fig. 2, which shows that melting begins at 563° under a pressure of 0·59 atmosphere. The final melting point has not yet been observed.

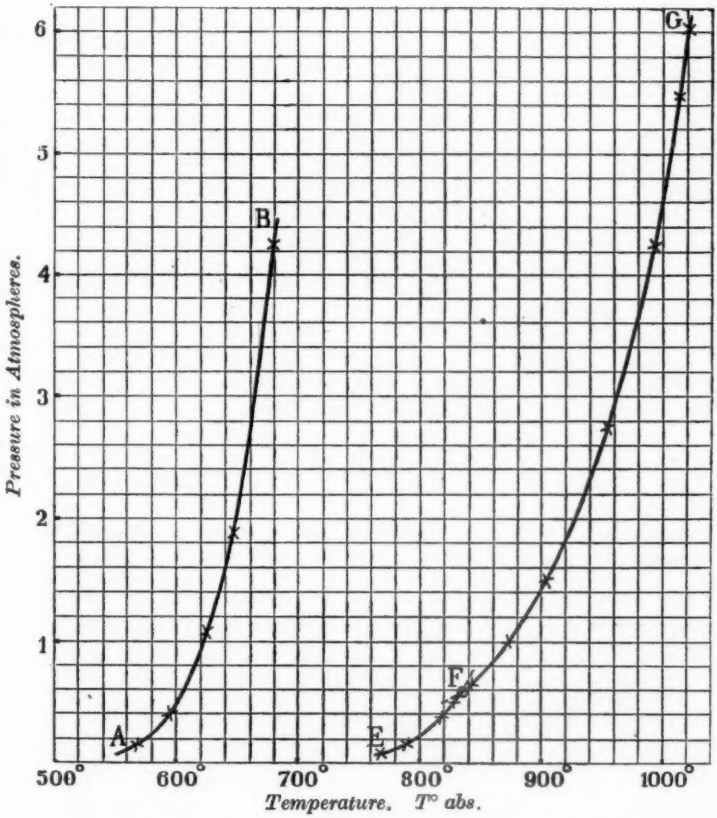
Drawing on a $P$–$T$ diagram the vapour pressure lines of preparation 1 and of the transformed state, we get Fig. 3.

This diagram may be compared with the $P$–$T$ diagram (Fig. 4) for the stable, metastable, and the liquid phases of a single substance, assumed to be monotropic.

TABLE II.

| $t°$. | $T°$ abs. | $p$=Pressure in cm. Hg. | $P$=Pressure in atmos. | $T \ln P$ or $2{\cdot}3025\, T \log_{10} P$. |
|---|---|---|---|---|
| 496 | 769° | 6·7 | 0·088 | −1867 |
| 517 | 790 | 12·4 | 0·163 | −1448 |
| 546 | 819 | 28·3 | 0·372 | − 809·1 |
| 556 | 829 | 37·1 | 0·488 | − 604·0 |
| 570 | 843 | 48·3 | 0·636 | − 382·3 |
| 600 | 873 | 76·9 | 1·012 | 10·05 |
| 632 | 905 | 113·3 | 1·490 | 360·4 |
| 681 | 954 | 209·3 | 2·754 | 966·3 |
| 723 | 996 | 325·4 | 4·282 | 1448 |
| 742 | 1015 | 417 | 5·486 | 1727 |
| 752 | 1025 | 458 | 6·027 | 1841 |

FIG. 3.

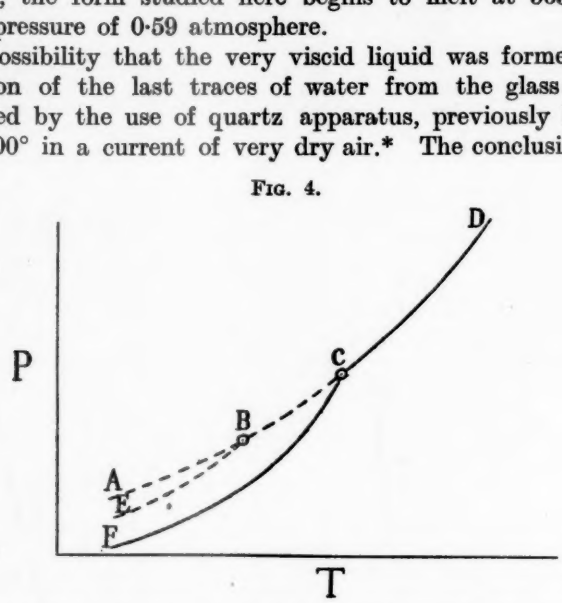



From Fig. 4, we see that the vapour pressure of the stable form at its melting point, C, is higher than the highest pressure of the solid metastable modification, that is, the pressure at its melting point, B.

In the case of phosphorus pentoxide the vapour pressure of the metastable form has been found to be more than 4 atmospheres at nearly 400°, a temperature still below the melting point of the low-pressure form. On the old considerations about the different states of aggregation, it would be expected that the vapour pressure at the melting point of the solid stable form would be still higher. Actually, the form studied here begins to melt at 563° with a vapour pressure of 0·59 atmosphere.

The possibility that the very viscid liquid was formed by the absorption of the last traces of water from the glass wall was eliminated by the use of quartz apparatus, previously heated to about 700° in a current of very dry air.* The conclusion, therefore, is that the appearance of the very viscous liquid signifies the beginning of melting, which is in complete contradiction to the old theory.

FIG. 4.




The explanation of the foregoing results offers no difficulty to the theory of allotropy, indeed the phenomena observed furnish valuable confirmation of the theory. The case of phosphorus pentoxide resembles that of sulphur trioxide (see preceding paper); for both substances, the crystalline state consists of mixed crystals, built up from molecules of different kinds. Only when the inner equilibrium is established does the pure substance behave as a real single one. If this equilibrium is established slowly, or if the transformations are stopped, then the pure substance behaves as a mixture. In a following paper the results of the continued study and the explanation of the observed phenomena will be given.

* To make sure of this, we are repeating the experiments after drying the quartz apparatus in another way.

*Summary.*

1. Vapour pressure determinations carried out with phosphorus pentoxide show that the volatility of the pure crystalline sublimate depends on the velocity of distillation. Thus, for example, the vapour pressures of two different preparations at 370° were 1·8 and 2·05 atmospheres, respectively. The vapour pressure is dependent on the previous history of the substance.

2. At 400°, the metastable sublimate changes into another modification, with a corresponding fall in vapour pressure from about 4 atmospheres to nearly zero. The volatility of the transformed modification is small and is dependent also on its previous history. According to the old theory, one should expect that the stable modification, into which the metastable form has passed, would melt at a higher vapour pressure than the highest exhibited by the metastable form. In contradiction to this, the transformed solid phase shows an initial melting point with a much lower vapour pressure, namely, 563° and 0·59 atmosphere. Moreover, it melts over a large temperature range. These observations can be interpreted on the basis of the theory of allotropy, *i.e.*, pure solid phosphorus pentoxide is to be regarded as a complex material.

THE UNIVERSITY, AMSTERDAM. [*Received, July 17th*, 1924.]

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## CCCLIII.—*Studies in Optical Superposition. Part VI. The Methyl-*n*-hexylcarbinyl Dimethoxysuccinates.*

By T. S. PATTERSON and CHARLES BUCHANAN.

IN previous parts of this investigation it has been shown that for the *l*-menthyl diacetyltartrates (J., 1907, **91**, 705), the *l*-menthylamine tartrates and the *l*-amyl dimethoxysuccinates (J., 1915, **107**, 142), and the *l*-octyl tartrates (this vol., p. 1475) the rotation of the *i*-form is not the same as the mean of the rotations of the *d*- and *l*-forms, but sometimes differs very widely from it, whereas, according to the principle of optical superposition, these two values should be identical.

This appears to us the simplest and most direct method of attacking the problem, but in recent years Hudson has published a number of interesting papers dealing with the sugars, and although we are not clear how far he himself considers his results to concern the principle of optical superposition, they are sometimes regarded as proving it, or at least as having a very important bearing on the subject, and for this reason we refer to them here. The relative data are shown in Table I.

TABLE I.

| Substance. | M.W. | $[M]_D$. α-form. | $[M]_D$. β-form. | $\Delta[M]_D$. |
|---|---|---|---|---|
| *d*-Glucose † | 180 | +204° | + 34° | +170° |
| *d*-Galactose † | 180 | 259 | 93 | 166 |
| Methyl-*d*-glucoside * | 194 | 305 | − 62 | 367 |
| Methyl-*d*-galactoside * | 194 | 379 | 0 | 379 |
| Ethyl-*d*-glucoside * | 208 | 314 | − 62 | 376 |
| Ethyl-*d*-galactoside * | 208 | 372 | − 8 | 380 |
| *d*-Mannose † | 180 | *61·2* | − 30·6 | 91·8 |
| *d*-Arabinose † | 150 | − *81* | −262 | 181 |
| *l*-Arabinose * | 150 | 114 | +276 | −162 |
| *d*-Xylose † | 150 | 138 | − *30* | +168 |
| *d*-Lyxose † | 150 | 8·2 | − *54* | 62·2 |
| Lactose † | 342 | 308 | +120 | 188 |
| Maltose † | 342 | *575* | 404 | 171 |
| Melibiose † | 342 | *612* | 424 | 188 |
| Cellose † | 342 | *246* | 55 | 191 |

* *J. Amer. Chem. Soc.*, 1909, **31**, 70. † *Ibid.*, 1917, **39**, 1035.

With regard to these data, several points must be noted. In the first place, the determination of the initial value for the rotation of such a substance as α- or β-glucose is a difficult operation, as indeed is indicated by the fact that in the earlier of the papers cited in Table I, Hudson quotes the molecular rotation of α-*d*-glucose, 196°, and of the β-form, 36°; similarly for galactose, he gives for the α-form, 252°, and for the β-form, 95°, whilst in the later paper he gives for the α-form of glucose, 204° *, and for the β-form, +34°; and for galactose, 259° and 93°, respectively. The differences in *molecular* rotation ($\Delta[M]_D$) thus become 169° instead of 160°, and 166° instead of 157°, quite considerable variations. The data for *d*- and *l*-arabinose illustrate the same difficulty. Since these substances are enantiomorphs, the data should be numerically the same, which is far from being the case.

Taking these data as they appear, however, Hudson, *assuming the principle of optical superposition*, regards the fact that the values of $\Delta[M]_D$ for the α- and the β-forms of glucose and galactose are nearly equal, as proving that the part of the rotation of these four molecules due to the aldehyde carbon atom is little affected by the difference in configuration of the remainder of the molecules. The same conclusion is reached from the fact that the values of $\Delta[M]_D$ for methyl-*d*-glucoside and methyl-*d*-galactoside are nearly equal, and similarly those for ethyl-*d*-glucoside and ethyl-*d*-galactoside. It must be noticed, however, that the values of $\Delta[M]_D$ for ethyl-*d*-glucoside and ethyl-*d*-galactoside agree better with the value for methyl-*d*-galactoside than the last-mentioned does with $\Delta[M]_D$

* He really gives the specific rotation. We have calculated it to molecular rotation.

for methyl-*d*-glucoside. The only valid conclusion to be drawn from these data is, we think, that there is no clearly perceptible difference between the effects of the methyl and ethyl groups. It may also be recalled that, as pointed out by one of us (J., 1915, **107**, 145), it is theoretically quite possible for a set of substances to show the behaviour exhibited by α- and β-*d*-glucose and α- and β-*d*-galactose, and yet to be entirely at variance with the principle of optical superposition.

Further, it will be observed, and indeed it has been pointed out by Hudson, that $\Delta[M]_D$ in the case of *l*-arabinose, in the case of *d*-xylose, in the case of α-glucoheptose, and even in lactose, maltose, mellibiose, and cellose, differs comparatively little from $\Delta[M]_D$ for glucose and galactose, from which it seems very apparent that large differences in the actual constitution—the number of carbon atoms—of these substances have very little effect upon the differences in the rotation of the α- and β-forms. In fact, there are two separate influences at work, (*a*) the number of carbon atoms in the molecule, and (*b*) the configuration of the groups about these carbon atoms; and if, when in passing from arabinose to lactose, an increase in the number of carbon atoms from five to twelve produces so little effect on the value of $\Delta[M]_D$, it is hardly to be expected that the effect of mere configuration in these cases should be any more apparent. Some of the data in the table have been arrived at by Hudson by an indirect method, which we think unlikely to give results accurate enough adequately to test a principle so subtle as this. They are shown in the table—as in Hudson's—in italics. Mannose is one of these substances, and, according to the principle of optical superposition, if the rotation of the aldehyde carbon atom is not affected by the configuration of the remainder of the molecule, then $\Delta[M]_D$ in the case of mannose should be the same as for glucose and for galactose. It varies widely, however, from what is required, being 92° instead of approximately 160°.

Again, the values of $\Delta[M]_D$ for *d*- and *l*-arabinose, which do not agree very well with one another, agree moderately well with xylose, but not at all with lyxose, with which, according to the principle of optical superposition, they should be identical.

Assuming Hudson's data to be correct, the only valid conclusion to be drawn is that the principle of optical superposition does not hold.

It may further be recalled that Hudson, a number of years ago, admitted some doubt as to whether the principle of optical superposition holds *exactly*, being of opinion that his figures showed it to hold at least closely (*J. Amer. Chem. Soc.*, 1909, **31**, 68, note). But more recently (*ibid.*, 1917, **39**, 462), in spite of this, he has

attempted to calculate the rotation due to each asymmetric carbon atom of the molecule of certain compounds, a procedure which necessarily assumes the principle to hold, not merely closely, but with rigorous mathematical exactitude. Still later, however, he remarks, *à propos* of mannose, " It appears, therefore, that the change from the glucose to the mannose chain does have considerable influence upon the rotatory power of the terminal asymmetric carbon atom " (*ibid.*, 1917, **39**, 1024). And again, " It appears probable, therefore, that the exceptional value of the difference for these sugars may be dependent upon this type of configuration " (*loc. cit.*, p. 1035). Now the whole question at issue is whether configuration does affect rotation, exactly in this sense, and if the data quoted by Hudson are even approximately correct, they, as a whole, contradict the principle of optical superposition. It remains true that Hudson's results are of great interest in the special cases with which he deals, but there is no meaning in the expression *Principle* of Optical Superposition unless it applies universally, and it would appear both from Hudson's work and our own that this is not the case; the requirements of van 't Hoff's proposition are sometimes fairly closely fulfilled, but in other cases are widely departed from. It will doubtless be admitted, however, that further work on the subject is very desirable.

We have therefore prepared and examined polarimetrically the di-*sec.*-octyl esters of *d*-, of *l*-, and of *i*-dimethoxysuccinic acid.

The resolution of the methyl-*n*-hexylcarbinol was carried out as described by Pickard and Kenyon (J., 1907, **71**, 2058; 1922, **121**, 2540). We used first the *l*-alcohol, which boiled at 80°/11 mm. and had the rotation $\alpha^{16°}_{5461}$ (200 mm.) = − 19·42°, the value given by Pickard and Kenyon being −19·40°. The alcohol was therefore considered to be pure.

The dimethoxysuccinic acids were prepared by the method described by Patterson and Patterson (J., 1915, **107**, 142), the *d*-acid from methyl *d*-tartrate and the other two from the silver salts of *l*- and of *i*-tartaric acids. The *d*-dimethoxysuccinic acid used, after recrystallisation from a mixture of acetone and benzene, melted at 155° and had the rotation $[\alpha]^{16°}_{5461} = +86·93$ (in water, $c = 1·783$); *l*-dimethoxysuccinic acid melted at 154° and had the rotation $[\alpha]^{16°}_{5461} = -86·93$ (in water, $c = 1·783$); the *i*-dimethoxysuccinic acid melted at 161°. The esters were prepared by passing dry hydrogen chloride through a mixture of the acid (1 mol.) and the alcohol (about 4 mols.) for 16 hours, keeping the temperature between 80° and 90°. The excess of alcohol was distilled up to 100°/40 mm., the residue dissolved in benzene, and the solution washed with dilute sodium carbonate solution, and with water.

After drying with calcium chloride, the bulk of the benzene was removed; the residue distilled under 4 mm. pressure; the main fraction redistilled and collected in two fractions. After the second distillation the rotation of the two fractions was practically the same and the substance therefore considered to be pure. The rotation of these esters was then examined at different temperatures and for different colours of light, both in the homogeneous condition and in solution.

The experimental data are collected at the end of the paper. As far as the question of optical superposition is concerned, they may be summarised as follows :

TABLE II.

Rotations for homogeneous esters at different temperatures.

| | $[\alpha]^{t°}_{5461}$. | | | | |
|---|---|---|---|---|---|
| $t°$. | *l-sec.*-Octyl *l*-dimethoxy-succinate. | *l-sec.*-Octyl *d*-dimethoxy-succinate. | Mean. | *l-sec.*-Octyl *i*-dimethoxy-succinate. | Diff. |
| 0° | −77·6° | +48·3° | −14·65° | −14·18° | 0·47° |
| 50 | 74·9 | 50·4 | 12·25 | 11·90 | 0·35 |
| 100 | 72·3 | 51·4 | 10·45 | 10·10 | 0·35 |
| 150 | 69·5 | 51·0 | 9·25 | 8·95 | 0·30 |

It will be noted from these figures that the rotations for the ester of the *i*-acid are different from the means of the rotations of the esters of the *d*- and *l*-acids. The difference is only slight, however, and perhaps not very far outside the limit of the experimental error. The fact that the difference varies consistently with change of temperature and that in all probability the variation would be in the opposite sense at higher temperatures favours the view that the results are not affected by any experimental error sufficient to obscure the effect of superposition.

Table III shows how the difference in rotation varies with change of wave-length for the homogeneous esters.

TABLE III.

$t = 20°$.

| λ. | *l-sec.*-Octyl *l*-dimethoxy-succinate. | *l-sec.*-Octyl *d*-dimethoxy-succinate. | Mean. | *l-sec.*-Octyl *i*-dimethoxy-succinate. | Diff. |
|---|---|---|---|---|---|
| 4358·3 | −123·4° | +80·25° | −21·67° | −20·50° | 1·17° |
| 4959·7 | 95·0 | 61·8 | 16·6 | 16·20 | 0·40 |
| 5460·7 | 76·7 | 49·3 | 13·7 | 13·15 | 0·55 |
| 5790·3 | 67·4 | 43·5 | 11·95 | 11·60 | 0·35 |
| 6234·3 | 58·4 | 37·4 | 10·5 | 10·15 | 0·35 |
| 6716·3 | 49·9 | 32·1 | 8·90 | 8·79 | 0·11 |

The esters were then examined as regards rotation in alcohol, *o*-nitrotoluene, and *s*-tetrachloroethane at various temperatures and for different colours of light. In Table IV are shown the data obtained in these three solvents at a concentration $c = 5$ and for the temperature 0°.

TABLE IV.

$[\alpha]^{0°}_{5461}$.

| Physical condition. | I. *l-sec.*-Octyl *l*-di-methoxy-succinate. | II. Solvent effect. | III. *l-sec.*-Octyl *d*-di-methoxy-succinate. | IV. Solvent effect. | V. Mean of I & III. | VI. *l-sec.*-Octyl *i*-di-methoxy-succinate. | VII. Solvent effect. | VIII. Δ V–VI. |
|---|---|---|---|---|---|---|---|---|
| Homogeneous ..... | −77·60° | | +48·30° | | −14·65° | −14·18° | | −0·47° |
| In alcohol ..... | −77·07 | + 0·53° | +52·67 | + 4·37° | −12·20 | − 9·52 | + 4·66° | −2·68 |
| In *o*-nitrotoluene ... | −96·0 | −18·40 | +85·00 | +36·70 | − 5·5 | − 2·25 | +11·93 | −3·25 |
| In *s*-tetrachloroethane ..... | −61·4 | +16·20 | +40·58 | − 7·72 | −10·41 | − 8·65 | + 5·53 | −1·76 |

It will be observed that the difference (col. VIII) between the rotation for the *i*-ester and the mean (col. V) of the rotations of the *d*- and *l*-esters is decidedly greater in solution than in the homogeneous condition. In *o*-nitrotoluene, it amounts to 3·25°, which, whilst not large in comparison with the range of 181° over which the rotations of the esters of the *d*- and *l*-acids extend, is numerically greater than the actual rotation (2·25°) of the ester of the *i*-acid. In the other two solvents used, the difference also seems clearly to be greater than the probable experimental error. The behaviour on change of temperature and colour of light is nearly the same as for the homogeneous substances.

It will also be observed from Table IV that these three liquids exercise a marked solvent influence on the active esters examined. The solvent effect (shown in cols. II, IV, and VII) is the change in rotation from that of the homogeneous ester due to solution, a change in the positive direction being marked + and *vice versa*.

The experiments detailed above involve the resolution of two potentially active compounds, *sec.*-octyl alcohol and racemic acid, as well as the preparation of *i*-tartaric acid, and since on this account the experimental error might be considerable, we thought it worth while to corroborate our results by preparing the esters corresponding to those described but from *d*-sec.-octyl alcohol instead of from *l*-sec.-octyl alcohol. The *d*.-sec.-octyl alcohol had a slightly higher rotation than the lævo, namely, $\alpha^{16°}_{5461}$ (200 mm.) +19·45° as against −19·42° for the lævo-alcohol and 19·40° of Pickard and Kenyon.

The various esters were prepared and purified as before, but were not so completely examined.

Table V gives a comparison of the results obtained.

## TABLE V.

Observed rotations of di-*sec.*-octyl esters of dimethoxysuccinic acids—Hg green—100 mm.—at 17°.

| | *l*-Acid. | *d*-Acid. | Mean. | *i*-Acid. | Δ. |
|---|---|---|---|---|---|
| *l-sec.*-Octyl esters ..... | −74·16° | +47·40° | −13·38° | −12·92° | −0·46° |
| *d-sec.*-Octyl esters ..... | −46·61 | +74·72 | +14·05 | +13·48 | +0·57 |
| Specific rotations in ethyl-alcoholic solution ($c = 5$) at 16° (approx.). | | | | | |
| *l-sec.*-Octyl esters ..... | −75·73 | +53·04 | −11·34 | −8·72 | −2·62 |
| *d-sec.*-Octyl esters ..... | −53·0 | +77·11 | +12·05 | +9·33 | +2·72 |
| Specific rotations in *o*-nitrotoluene solution ($c = 5$) at 14°—Hg green. | | | | | |
| *l-sec.*-Octyl esters ..... | −92·04 | +81·25 | −5·57 | −3·12 | −2·45 |
| *d-sec.*-Octyl esters ..... | −80·7 | +93·40 | +6·35 | +3·10 | +3·25 |
| Specific rotations in *s*-tetrachloroethane solution ($c = 5$) at 18°. | | | | | |
| *l-sec.*-Octyl esters ..... | −61·5 | +41·6 | − 9·95 | −8·55 | −1·40 |
| *d-sec.*-Octyl esters ..... | −40·5 | +61·92 | +10·71 | +8·35 | +2·36 |

In the table, the data for *observed* rotation are compared in the case of the homogeneous esters, as the densities of the *d-sec.*-octyl esters were not determined. Previous work has shown that any influence due to difference in the densities would be negligible.

It will be seen that the results agree closely with those obtained with the *l*-alcohol. The difference between the rotation of the ester of the *i*-acid and the mean of the rotations ($\lambda = 5461$) for the homogeneous esters of the *d*- and *l*-acids in the second series of experiments is 0·57° as against 0·46°; in alcohol solution, it is 2·72° as against 2·62°; in nitrotoluene, 3·25° as against 2·45°; and in tetrachloroethane, it is 2·36° as against 1·40°.

The behaviour of the two series is entirely consistent; and although the departure from the requirements of the principle of optical superposition is small compared with what it has been found to be in some other cases, it appears to be quite definite.

## EXPERIMENTAL.

The colours of light used were the following and, to save space, will be denoted in the sequel by letters.

| | $r_1$. | $r_2$. | y. | g. | b. | v. |
|---|---|---|---|---|---|---|
| $\lambda =$ | 6716·3 | 6234·3 | 5790·3 | 5460·7 | 4959·7 | 4358·3 |

l-sec.-*Octyl* d-*dimethoxysuccinate* was prepared as described above. In the final distillation, a small first fraction, collected separately, had rotation in 100 mm. tube $\alpha_{5461}^{13\cdot5^\circ} = +47\cdot5^\circ$, and the main portion $\alpha_{5461}^{13\cdot5^\circ} = +47\cdot415^\circ$. B p. = 196°/4 mm.

| $t°$. | $d$. | $a_{r_1}$ (50 mm.). | $[a]_{r_1}$. | $a_{r_2}$. | $[a]_{r_2}$. | $a_y$. | $[a]_y$. | $a_g$. | $[a]_g$. | $a_b$. | $[a]_b$. | $a_v$. | $[a]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·9794 | +15·328° | +31·30° | +17·97° | +36·70° | +20·91° | +42·70° | +23·64° | +48·27° | +29·50° | +60·24° | +38·18° | +77·97° |
| 12·5 | 0·9691 | 15·345 | 31·66 | 17·98 | 37·11 | 21·01 | 43·36 | 23·70 | 48·88 | 29·77 | 61·43 | 38·48 | 79·40 |
| 43·0 | 0·9449 | 15·315 | 32·42 | 17·90 | 37·89 | 20·945 | 44·33 | 23·78 | 50·33 | 29·84 | 63·16 | 39·01 | 82·57 |
| 68·8 | 0·9244 | 15·09 | 32·65 | 17·75 | 38·40 | 20·76 | 44·91 | 23·54 | 50·92 | 29·65 | 64·14 | 39·00 | 84·38 |
| 100 | 0·9001 | 14·69 | 32·62 | 17·33 | 38·48 | 20·30 | 45·08 | 23·06 | 51·21 | 29·18 | 64·81 | 38·60 | 85·72 |
| 147·5 | 0·8649 | 14·01 | 32·39 | 16·50 | 38·15 | 19·40 | 43·84 | 22·06 | 51·01 | 28·12 | 65·01 | 37·30 | 86·24 |

Ethyl-alcoholic solution : $p = 6\cdot210$.

*Densities* determined : 0·8068 at 11·5°; 0·7925 at 30°; 0·7816 at 42·8°; 0·7724 at 52·8°.

| $t°$. | $d$. | $a_{r_1}$ (160 mm.). | $[a]_{r_1}$. | $a_{r_2}$. | $[a]_{r_2}$. | $a_y$. | $[a]_y$. | $a_g$. | $[a]_g$. | $a_b$. | $[a]_b$. | $a_v$. | $[a]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·8185 | +2·753° | +33·84° | +3·23° | +39·49° | +3·84° | +47·00° | +4·285° | +52·67° | +5·37° | +66·00° | +6·935° | +85·24° |
| 16 | 0·8045 | 2·735 | 34·22 | 3·185 | 39·85 | 3·742 | 46·81 | 4·24 | 53·04 | 5·295 | 66·24 | 6·885 | 86·93 |

*s*-Tetrachloroethane solution : $p = 3\cdot1868$.

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 1·5972 | +2·123 | +26·07 | +2·487 | +30·54 | +2·89 | +35·49 | +3·305 | +40·58 | +4·035 | +49·55 | +5·218 | +64·07 |
| 14·5 | 1·5759 | 2·182 | 27·16 | 2·535 | 31·40 | 2·97 | 36·96 | 3·328 | 41·42 | 4·18 | 52·02 | 5·23 | 65·09 |
| 43·5 | 1·5328 | 2·23 | 28·53 | 2·565 | 32·82 | 2·992 | 38·28 | 3·43 | 43·89 | 4·27 | 54·64 | 5·568 | 71·24 |
| 75·0 | 1·4853 | 2·186 | 28·87 | 2·525 | 33·34 | 2·922 | 38·58 | 3·40 | 44·90 | 4·255 | 56·19 | 5·58 | 73·68 |
| 98·5 | 1·4485 | 2·178 | 29·49 | 2·50 | 33·85 | 2·95 | 39·94 | 3·35 | 45·36 | 4·212 | 57·03 | 5·545 | 75·08 |

*o*-Nitrotoluene solution : $p = 4\cdot3205$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 1·1702 | +4·368 | +54·00 | +5·13 | +63·42 | +6·04 | +74·66 | +6·895 | +85·24 | +8·744 | +108·09 |
| 17·8 | 1·1540 | 4·11 | 51·64 | 4·79 | 60·18 | 5·66 | 71·12 | 6·41 | 80·54 | 8·09 | 101·65 |
| 45·0 | 1·1296 | 3·67 | 46·98 | 4·292 | 54·95 | 5·039 | 64·50 | 5·78 | 74·00 | 7·298 | 93·43 |
| 75·0 | 1·1008 | 3·328 | 43·75 | 3·882 | 51·02 | 4·544 | 59·85 | 5·19 | 67·20 | 6·56 | 86·21 |
| 100 | 1·0765 | 3·055 | 41·05 | 3·57 | 47·97 | 4·254 | 57·17 | 4·795 | 64·44 | 6·027 | 80·99 |

l-sec.-*Octyl* l-*dimethoxysuccinate* was prepared from 10 g. of *l*-dimethoxysuccinic acid and 35 g. of *l-sec.*-octyl alcohol

l-sec.-*Octyl* l-*dimethoxysuccinate* was prepared from 10 g. of *l*-dimethoxysuccinic acid and 35 g. of *l-sec.*-octyl alcohol and treated exactly as above. The b. p. was 190°/ about 4 mm. A small first fraction in the final distillation had rotation $\alpha^{16°}_{5461} = -74{\cdot}22°$ (100 mm.) and the main fraction $\alpha^{17°}_{5461} = -74{\cdot}105°$.

| $t°$. | $d$. | $a_{r_1}$ (50 mm.). | $[a]_{r_1}$. | $a_{r_2}$. | $[a]_{r_2}$. | $a_y$. | $[a]_y$. | $a_g$. | $[a]_g$. | $a_b$. | $[a]_b$. | $a_v$. | $[a]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·9764 | −24·925° | −51·06° | −28·85° | −59·09° | −33·495° | −68·61° | −37·835° | −77·50° | −46·772° | −95·81° | −60·506° | −124·6° |
| 14 | 0·9653 | 24·088 | 49·81 | 28·235 | 58·37 | 32·835 | 67·53 | 37·135 | 76·94 | 46·15 | 95·62 | 59·66 | 123·61 |
| 43 | 0·9430 | 23·099 | 48·99 | 26·987 | 57·24 | 31·535 | 65·72 | 35·73 | 75·78 | 44·545 | 94·48 | 57·605 | 122·17 |
| 77·5 | 0·9162 | 21·923 | 47·86 | 25·535 | 55·75 | 29·819 | 65·09 | 33·82 | 73·84 | 42·08 | 91·87 | 54·94 | 119·94 |
| 100 | 0·8984 | 21·18 | 47·15 | 24·645 | 54·86 | 28·66 | 63·76 | 32·555 | 72·47 | 40·649 | 90·49 | 53·033 | 118·06 |
| 147·5 | 0·8613 | 20·378 | 47·32 | 22·63 | 52·55 | 26·439 | 61·39 | 29·995 | 69·65 | 37·498 | 86·07 | 49·038 | 115·03 |

Ethyl-alcoholic solution : $p = 6{\cdot}229$.

*Densities* determined : 0·8052 at 13°; 0·7935 at 27°; 0·7846 at 37·2°; 0·7766 at 47°.

| $t°$. | $d$. | $a_{r_1}$ (160 mm.). | $[a]_{r_1}$. | $a_{r_2}$. | $[a]_{r_2}$. | $a_y$. | $[a]_y$. | $a_g$. | $[a]_g$. | $a_b$. | $[a]_b$. | $a_v$. | $[a]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·8163 | −4·173° | −51·29° | −4·814° | −59·17° | −5·568° | −68·44° | −6·27° | −77·07° | −7·805° | −95·93° | −9·963° | −122·5° |
| 16·5 | 0·8022 | 4·018 | 50·25 | 4·627 | 57·87 | 5·380 | 67·29 | 6·055 | 75·73 | 7·513 | 93·97 | 9·626 | 120·4 |

*s*-Tetrachloroethane solution : $p = 3{\cdot}1896$.

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1·5972 | −3·336 | −40·92 | −3·85 | −47·23 | −4·436 | −54·42 | −5·005 | −61·40 | −6·154 | −75·50 | −7·782 | −95·47 |
| 14 | 1·5765 | 3·285 | 40·83 | 3·785 | 47·05 | 4·39 | 54·57 | 4·94 | 61·40 | 6·084 | 75·80 | 7·635 | 94·91 |
| 43 | 1·5335 | 3·17 | 40·51 | 3·628 | 46·36 | 4·24 | 53·18 | 4·748 | 60·67 | 5·815 | 74·30 | 7·631 | 97·51 |
| 71 | 1·4915 | 3·007 | 39·51 | 3·38 | 44·41 | 4·035 | 53·01 | 4·565 | 59·97 | 5·666 | 74·44 | 7·27 | 95·51 |
| 100 | 1·4465 | 2·917 | 39·52 | 3·368 | 45·62 | 3·888 | 52·67 | 4·406 | 59·68 | 5·51 | 74·64 | 7·02 | 95·10 |

*o*-Nitrotoluene solution : $p = 4{\cdot}3394$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1·1702 | −5·035 | −61·97 | −5·782 | −71·17 | −6·787 | −83·54 | −7·805 | −96·06 | −10·026 | −123·57 |
| 16 | 1·1560 | 4·738 | 59·17 | 5·52 | 68·94 | 6·444 | 80·47 | 7·36 | 91·91 | 9·495 | 118·57 |
| 42·8 | 1·1312 | 4·404 | 56·08 | 5·065 | 64·50 | 5·954 | 75·82 | 6·775 | 86·27 | 8·646 | 110·10 |
| 73·2 | 1·1028 | 3·992 | 52·14 | 4·65 | 60·73 | 5·408 | 70·63 | 6·18 | 80·71 | 7·807 | 101·96 |
| 100 | 1·0765 | 3·75 | 50·17 | 4·32 | 57·80 | 5·035 | 67·37 | 5·76 | 77·07 | 7·266 | 97·22 |

l-sec.-*Octyl* i-*dimethoxysuccinate* distilled at 199—201°/4 mm. The first fraction in the final distillation had rotation in 100 mm. tube $\alpha^{18°}_{5461} = -12{\cdot}72°$ and the main fraction $\alpha^{18{\cdot}5°}_{5461} = -12{\cdot}687°$ (Found: C = 65·40; H = 10·52. Calc., C = 65·67; H = 10·45%).

| $t°$. | $d$. | $\alpha_{r_1}$ (50 mm.). | $[\alpha]_{r_1}$. | $\alpha_{r_2}$. | $[\alpha]_{r_2}$. | $\alpha_y$. | $[\alpha]_y$. | $\alpha_g$. | $[\alpha]_g$. | $\alpha_b$. | $[\alpha]_b$. | $\alpha_v$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·9775 | −4·601° | −9·41° | −5·325° | −10·88° | −6·085° | −12·45° | −6·925° | −14·17° | −8·569° | −17·53° | −10·825° | −22·148° |
| 16·2 | 0·9646 | 4·29 | 8·90 | 4·963 | 10·29 | 5·685 | 11·79 | 6·401 | 13·27 | 7·907 | 16·39 | 10·02 | 20·78 |
| 42 | 0·9437 | 3·845 | 8·15 | 4·40 | 9·33 | 5·075 | 10·76 | 5·73 | 12·15 | 7·072 | 14·99 | 8·905 | 18·87 |
| 73 | 0·9189 | 3·387 | 7·37 | 3·90 | 8·49 | 4·475 | 9·74 | 5·025 | 10·94 | 6·164 | 13·42 | 7·71 | 16·78 |
| 100 | 0·8973 | 3·035 | 6·76 | 3·495 | 7·79 | 4·045 | 9·02 | 4·50 | 10·03 | 5·478 | 12·22 | 6·89 | 15·36 |
| 127·2 | 0·8756 | 2·819 | 6·44 | 3·225 | 7·37 | 3·678 | 8·40 | 4·14 | 9·59 | 5·071 | 11·58 | 6·365 | 14·54 |
| 150·2 | 0·8572 | 2·589 | 6·04 | 2·977 | 6·95 | 3·41 | 7·96 | 3·815 | 8·90 | 4·633 | 10·81 | 5·766 | 13·45 |

Ethyl-alcoholic solution: $p = 6{\cdot}230$.

*Densities* determined: 0·8027 at 15°, 0·7938 at 27°, 0·7853 at 37·2°, 0·7745 at 49·5°.

| $t°$. | $d$. | $\alpha_{r_1}$ (160 mm.). | $[\alpha]_{r_1}$. | $\alpha_{r_2}$. | $[\alpha]_{r_2}$. | $\alpha_y$. | $[\alpha]_y$. | $\alpha_g$. | $[\alpha]_g$. | $\alpha_b$. | $[\alpha]_b$. | $\alpha_v$. | $[\alpha]_v$. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 0·8170 | −0·561° | −6·89° | −0·619° | −7·76° | −0·689° | −8·46° | −0·775° | −9·52° | −0·886° | −10·91° | −1·063° | −13·056° |
| 16·5 | 0·8028 | 0·512 | 6·28 | 0·555 | 6·94 | 0·613 | 7·67 | 0·697 | 8·72 | 0·849 | 10·62 | 0·998 | 12·48 |

*s*-Tetrachloroethane solution: $p = 3{\cdot}1889$.

| | | | | |
|---|---|---|---|---|
| $t$ | 0° | 15° | 44·2° | 72·5° | 100° |
| $d$ | 1·5972 | 1·5751 | 1·5316 | 1·4890 | 1·4465 |
| $\alpha_g$ (160 mm.) | −0·705° | −0·69° | −0·655° | −0·58° | −0·526° |
| $[\alpha]_g$ | −8·65° | −8·59° | −8·38° | −7·63° | −7·13° |

*o*-Nitrotoluene solution: $p = 4{\cdot}3407$.

| $t°$. | $d$. | $\alpha_{r_1}$ (160 mm.). | $[\alpha]_{r_1}$. | $\alpha_{r_2}$. | $[\alpha]_{r_2}$. | $\alpha_y$. | $[\alpha]_y$. | $\alpha_g$. | $[\alpha]_g$. | $\alpha_b$. | $[\alpha]_b$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0° | 1·1702 | −0·151° | −1·86° | −0·16° | −1·97° | −0·164° | −2·02° | −0·18° | −2·215° | −0·241° | −2·97° |
| 16 | 1·1560 | 0·197 | 2·46 | 0·218 | 2·72 | 0·247 | 3·08 | 0·27 | 3·37 | 0·341 | 4·26 |
| 52 | 1·1230 | 0·26 | 3·33 | 0·28 | 3·59 | 0·319 | 4·09 | 0·355 | 4·55 | 0·44 | 5·64 |
| 79 | 1·0972 | 0·265 | 3·48 | 0·30 | 3·94 | 0·327 | 4·29 | 0·362 | 4·75 | 0·476 | 6·24 |
| 100 | 1·0765 | 0·274 | 3·66 | 0·297 | 3·97 | 0·32 | 4·28 | 0·358 | 4·79 | 0·468 | 6·26 |

d-sec.-*Octyl* d-*dimethoxysuccinate* was prepared as above, from 6 g. of *d*-dimethoxysuccinic acid and 16 g. of *d-sec.*-octyl alcohol. It distilled at 202°/5 mm., a first small fraction being collected separately; the main portion had observed rotation in 100 mm. tube $\alpha^{19°}_{5461} = +74{\cdot}62°$. This was redistilled and a small fraction again collected separately; the rotation of the main fraction was now $\alpha^{17°}_{5461} = 74{\cdot}72°$ (Found: C = 65·45; H = 10·41. Calc., C = 65·67; H = 10·45%).

d-sec.-*Octyl* l-*dimethoxysuccinate* was prepared in the same manner. It distilled at 194°/approx. 4 mm. Rotation $\alpha^{15·5°}_{5461} = -46{\cdot}56°$. After redistillation, rotation was $\alpha^{17°}_{5461} = -46{\cdot}61°$ (Found: C = 65·33; H = 10·50%).

d-sec.-*Octyl* i-*dimethoxysuccinate*, prepared as above, had b. p. 202°/5 mm., $\alpha^{12·5°}_{5461} = +13{\cdot}71°$, and after redistillation $\alpha^{13°}_{5461} = 13{\cdot}67°$ (Found: C = 65·27; H = 10·46%).

The solutions of the esters of the *d*-alcohol were prepared by weighing out, as nearly as possible, 0·25 g. of the ester and making up to 5 c.c. with the solvent. (As a check, the solution was then weighed and the specific rotation calculated using the density of the corresponding solution of the *l*-alcohol esters; the specific rotations so calculated did not differ appreciably from the rotations calculated using only the mass per 100 c.c.).

| | Solvent. | c. | Obs. rot. Hg green. 100 mm. | Temp. | Specific rotation. |
|---|---|---|---|---|---|
| *d-sec.*-Octyl *l*-dimethoxysuccinate | Alcohol | 5 | −2·65° | 16° | −53·0° |
| | *o*-Nitrotoluene | 5 | −3·96 | 20 | −79·2 |
| | *s*-Tetrachloroethane | 5·008 | −2·025 | 20 | −40·43 |
| *d-sec.*-Octyl *d*-dimethoxysuccinate | Alcohol | 5·012 | +3·865 | 15 | +77·11 |
| | *o*-Nitrotoluene | 5·014 | +4·685 | 14·2 | +93·44 |
| | *s*-Tetrachloroethane | 4·992 | +3·092 | 16 | +61·92 |
| *d-sec.*-Octyl *i*-dimethoxysuccinate | Alcohol | 5·004 | +0·467 | 16·5 | + 9·33 |
| | *o*-Nitrotoluene | 5·012 | +0·16 | 16·5 | + 3·19 |
| | *s*-Tetrachloroethane | 5·008 | +0·418 | 18 | + 8·35 |

Analysis :—About 0·5 g. of each ester was hydrolysed by boiling with a standard solution of caustic soda in methyl alcohol, with the addition of a little water, for about an hour, and the excess caustic soda was titrated with standard hydrochloric acid solution. N.F. of NaOH solution = 0·2004.

| | | Gm. of ester. | C.c. of NaOH solution used. | Theoretical. C.c. |
|---|---|---|---|---|
| *l-sec.*-Octyl | *l*-dimethoxysuccinate | 0·4200 | 10·31 | 10·42 |
| | *d*- ,, | 0·4825 | 12·03 | 11·98 |
| | *i*- ,, | 0·4785 | 11·9 | 11·95 |
| *d-sec.*-Octyl | *d*- ,, | 0·4583 | 11·6 | 11·4 |
| | *l*- ,, | 0·3047 | 7·66 | 7·57 |
| | *i*- ,, | 0·2407 | 6·07 | 5·98 |

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ORGANIC CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW. [*Received, July 3rd*, 1924.]

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## CCCLIV.—*The Velocity of Reaction in Mixed Solvents. Part VII. The Influence of the Base on the Velocity of Saponification of Esters in Methyl Alcohol–Water Mixtures.*

By WALTER IDRIS JONES, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH.

IN a previous communication (J., 1923, **123**, 2688) the velocity of saponification of certain methyl esters by potassium hydroxide in methyl alcohol–water mixtures at 30° was studied. The work has been extended to a study of the effects caused by a change in the base; lithium hydroxide, barium hydroxide, and tetramethylammonium hydroxide were chosen in order that a comparison might be made with the effects observed in the case of ethyl esters (J., 1923, **123**, 197).

An examination of the results shows that the curves are divisible into linear sections and that the deviation of the observed value of $k$ from that required by a straight line is within the experimental error. The following figures were obtained in the case of methyl *o*-chlorobenzoate and barium hydroxide :

| Per cent. alcohol. | 90 | 85 | 82·5 | 80 | 75 | 70 |
|---|---|---|---|---|---|---|
| $k$ observed ..... | 0·100 | 0·133 | 0·155 | 0·166 | 0·203 | 0·235 |
| $k$ calculated ..... | 0·100 | 0·136 | 0·152 | 0·167 | 0·204 | 0·235 |

The points at which the linear sections would intersect have been calculated or deduced from the curves; the mean values are given in Table I :

TABLE I.

| Base. | Points of inflexion (per cent. alcohol) at 30°. | | | | |
|---|---|---|---|---|---|
| KOH ..... | 79 | 63·6 | | 47·7 | 36·7 |
| LiOH ..... | 78 | | 54 | | 37·3 |
| $Ba(OH)_2$ ..... | 78·1 | 63·5 | | 48·6 | 37·5 |
| $NMe_4OH$ ... | 76·8 | 63·8 | | 47·7 | 36·7 |

It will be seen that all four bases give points of inflexion at 77·8 and at 37·25% methyl alcohol, compositions corresponding to the complexes $2CH_3{\cdot}OH,H_2O$ and $CH_3{\cdot}OH,3H_2O$; lithium hydroxide differs from the other bases in yielding a point of inflexion at 54%

methyl alcohol corresponding to the complex $2CH_3{\cdot}OH,3H_2O$, whereas the other bases give points of inflexion corresponding to the complexes $CH_3{\cdot}OH,H_2O$ and $CH_3{\cdot}OH,2H_2O$.

A comparison of these results with those obtained with the ethyl esters shows that in each case tetra-alkylammonium hydroxide and potassium hydroxide gave almost identical results and that lithium hydroxide differed from the other two bases in a similar manner.

The dissimilarity in behaviour of the bases is of interest, as it would seem to indicate that the process of saponification is not mainly promoted by hydroxyl ions but is brought about by the formation of a complex between the ester and the base and its subsequent decomposition. It might be expected that methyl alcohol would tend to favour an ionic reaction and some evidence is drawn from the results in accord with this view. If the values of $k$ in ethyl alcohol–water mixtures containing more than 55% of water are compared for the different bases, it is found that there is little resemblance between them and the relative strengths of the bases, whereas in the case of methyl alcohol–water mixtures there is a very close agreement.

An examination of the relative velocity coefficients for each percentage of alcohol allows some very interesting conclusions to be drawn. The ratio $k_{KOH}/k_{base}$ has been calculated and the results are shown in Table II :

TABLE II.

| | Methyl *n*-butyrate. | | | Methyl *o*-chlorobenzoate. | | |
|---|---|---|---|---|---|---|
| Per cent. alcohol. | $k_{KOH}/k_{LiOH}$. | $k_{KOH}/k_{Ba(OH)_2}$. | $k_{KOH}/k_{NMe_4{\cdot}OH}$. | $k_{KOH}/k_{LiOH}$. | $k_{KOH}/k_{Ba(OH)_2}$. | $k_{KOH}/k_{NMe_4{\cdot}OH}$. |
| 90 | 0·90 | 0·47 | 1·33 | 0·96 | 0·25 | 1·38 |
| 85 | 0·92 | 0·61 | 1·31 | 0·97 | 0·34 | 1·32 |
| 82·5 | 0·87 | 0·57 | 1·14 | 0·90 | 0·35 | 1·21 |
| 80 | 0·89 | 0·60 | 1·90 | 0·92 | 0·36 | 1·06 |
| 75 | 0·96 | 0·73 | 1·09 | 1·00 | 0·50 | 1·14 |
| 70 | 0·97 | 0·80 | 1·12 | 0·90 | 0·56 | 1·05 |
| 65 | — | 0·73 | 1·10 | — | — | 1·15 |
| 62·75 | 0·99 | 0·96 | 1·14 | 1·00 | 0·81 | 1·15 |
| 60 | 1·19 | 1·06 | 1·08 | 0·93 | 0·85 | 1·13 |
| 55 | 1·23 | 0·93 | 1·10 | 1·22 | 0·81 | 1·12 |
| 50 | 1·12 | 0·89 | 1·10 | 1·18 | 0·80 | 1·14 |
| 45 | 1·00 | 0·89 | 0·94 | 1·14 | 0·87 | 1·07 |
| 40 | 1·16 | 0·96 | 1·09 | 1·09 | 0·87 | 1·05 |
| 35 | 1·52 | 1·00 | 1·15 | 1·13 | 0·84 | 0·98 |
| 32·75 | 1·78 | 1·29 | 1·48 | 1·14 | 0·85 | 1·08 |
| 30 | 2·37 | 1·76 | 2·11 | 1·31 | 0·97 | 1·21 |

The ratio for lithium hydroxide seems to be divisible into two sections, one in which the ratio is about 0·94 and the methyl alcohol is of greater concentration than 65%, and the second in which the ratio is about 1·16 and the concentration of the alcohol is less than

60%. This latter ratio is also the ratio of the reactivities of the bases. In the case of ethyl alcohol–water mixtures a constant ratio of 1·09 was found.

In the case of barium hydroxide the ratios show that the reactivity of the base is increasingly greater as the percentage of alcohol rises above 65. This effect would also seem to be dependent upon the nature of the ester, since the figures for the two esters are not comparable.

If the ratio $k_{\text{methyl } n\text{-butyrate}}/k_{\text{methyl } o\text{-chlorobenzoate}}$ is calculated, it is found that in methyl alcohol–water mixtures containing more than 62·75% of alcohol the value decreases regularly from 1·0 to 0·56; as the percentage of water is increased, the ratio assumes a value of 1·13, a value found in the case of the other bases.

Tetramethylammonium hydroxide gives a ratio which is appreciably constant at 1·12, but there is a tendency, in solvents containing over 85% of alcohol, for this value to increase to 1·38. This result is almost identical with that obtained in the case of ethyl alcohol–water mixtures.

A consideration of the values of the ratios in solvents rich in alcohol would seem to lend support to the views brought forward previously (J., 1923, **123**, 200). If the velocity of saponification is governed by the rate of formation of a complex between the ester and that proportion of the base existing as hydroxide, and the complex between the ester and that proportion of the base existing as methoxide is relatively very stable, then the velocity of saponification is dependent upon two factors. First, the relative proportions of the base existing as hydroxide and methoxide and, secondly, a steric factor which includes both the influence of the ester and the base. Lithium hydroxide and tetramethylammonium hydroxide yield results which are in accord with these views. In the case of barium hydroxide and methyl *n*-butyrate a small value for the ratio might be expected, since it is known that this base shows little tendency to form a methoxide compared with potassium hydroxide. In the case of barium hydroxide and methyl *o*-chlorobenzoate it would be expected that the presence of an ortho-substituent would increase the influence of the steric factor and the value of the ratio would consequently be greater than in the case of the *n*-butyrate; the reverse is the case and the ratio is very markedly smaller. This behaviour is associated with the absence of a point of inflexion at 77·8% alcohol.

## EXPERIMENTAL.

The solvents and the esters were prepared in the usual manner. The experiments with lithium hydroxide and with tetramethylammonium hydroxide were carried out as previously described.

## TABLE III.

### Lithium hydroxide and methyl *n*-butyrate.

| % alcohol. | $c_{LiOH}$. | $c_{ester}$. | Limit $k$. | $k$. |
|---|---|---|---|---|
| 90 | 0·06901 | 0·04444 | 0·0275—0·031 | 0·029 |
| 85 | 0·06700 | ,, | 0·053 —0·056 | 0·0545 |
| 82·5 | 0·07467 | 0·03333 | 0·063 —0·068 | 0·066 |
| 80 | 0·05576 | ,, | 0·076 —0·079 | 0·0775 |
| 75 | 0·03456 | 0·02222 | 0·112 —0·117 | 0·115 |
| 70 | 0·03748 | 0·01666 | 0·165 —0·180 | 0·170 |
| 62·75 | 0·02256 | 0·01333 | 0·245 —0·260 | 0·255 |
| 60 | 0·02043 | ,, | 0·27 —0·29 | 0·28 |
| 55 | 0·02176 | ,, | 0·335 —0·365 | 0·355 |
| 50 | 0·01720 | 0·00833 | 0·515 —0·545 | 0·53 |
| 45 | 0·01833 | ,, | 0·71 —0·74 | 0·73 |
| 40 | 0·01885 | ,, | 0·90 —0·94 | 0·92 |
| 35 | 0·01295 | 0·00583 | 1·26 —1·37 | 1·31 |
| 32·8 | 0·01331 | ,, | 1·50 —1·70 | 1·60 |
| 30 | 0·01441 | ,, | 1·85 —1·95 | 1·90 |

## TABLE IV.

### Lithium hydroxide and methyl *o*-chlorobenzoate.

| % alcohol. | $c_{LiOH}$. | $c_{ester}$. | Limit $k$. | $k$. |
|---|---|---|---|---|
| 90 | 0·06901 | 0·04444 | 0·025 —0·028 | 0·026 |
| 85 | 0·06700 | ,, | 0·045 —0·047 | 0·0465 |
| 82·5 | 0·07467 | 0·03333 | 0·0585—0·061 | 0·059 |
| 80 | 0·03830 | 0·03636 | 0·065 —0·067 | 0·0665 |
| 75 | 0·03456 | 0·02222 | 0·096 —0·101 | 0·0985 |
| 70 | 0·03748 | 0·01666 | 0·135 —0·150 | 0·145 |
| 62·75 | 0·02256 | 0·01333 | 0·200 —0·210 | 0·205 |
| 60 | 0·02043 | ,, | 0·215 —0·23 | 0·225 |
| 55 | 0·02176 | ,, | 0·285 —0·300 | 0·290 |
| 50 | 0·01720 | 0·00833 | 0·395 —0·425 | 0·41 |
| 45 | 0·01890 | ,, | 0·575 —0·580 | 0·575 |
| 40 | 0·01885 | ,, | 0·75 —0·79 | 0·77 |
| 35 | 0·01373 | 0·00583 | 1·15 —1·25 | 1·18 |
| 32·8 | 0·01331 | ,, | 1·35 —1·45 | 1·38 |
| 30 | 0·01441 | ,, | 1·65 —1·75 | 1·73 |

## TABLE V.

### Tetramethylammonium hydroxide and methyl *n*-butyrate.

| % alcohol. | $c_{NMe_4OH}$. | $c_{ester}$. | Limit $k$. | $k$. |
|---|---|---|---|---|
| 90 | 0·03256 | 0·02222 | 0·018—0·021 | 0·0195 |
| 85 | 0·05060 | ,, | 0·037—0·0385 | 0·038 |
| 82·5 | 0·04582 | 0·02500 | 0·049—0·051 | 0·050 |
| 80 | 0·04890 | ,, | 0·062—0·064 | 0·063 |
| 75 | 0·03148 | 0·02222 | 0·099—0·104 | 0·102 |
| 70 | 0·03372 | 0·01666 | 0·14 —0·15 | 0·147 |
| 65 | 0·03551 | ,, | 0·195—0·203 | 0·198 |
| 62·75 | 0·02082 | 0·01333 | 0·215—0·225 | 0·220 |
| 60 | 0·02205 | ,, | 0·305—0·315 | 0·310 |
| 55 | 0·02244 | ,, | 0·390—0·41 | 0·405 |
| 50 | 0·01632 | 0·00833 | 0·530—0·555 | 0·535 |
| 45 | 0·01651 | ,, | 0·76 —0·80 | 0·78 |
| 42·5 | 0·01686 | ,, | 0·88 —0·92 | 0·895 |
| 40 | 0·01712 | ,, | 0·96 —1·00 | 0·98 |
| 37·5 | 0·01852 | 0·00583 | 1·48 —1·57 | 1·54 |
| 35 | 0·01238 | ,, | 1·65 —1·75 | 1·72 |
| 32·8 | 0·01227 | ,, | 1·85 —1·95 | 1·93 |
| 30 | 0·01240 | ,, | 2·05 —2·20 | 2·14 |

## TABLE VI.

Tetramethylammonium hydroxide and methyl *o*-chlorobenzoate.

| % alcohol. | $c_{NMe_4\cdot OH}$. | $c_{ester}$. | Limit *k*. | *k*. |
|---|---|---|---|---|
| 90 | 0·03256 | 0·02222 | 0·0175—0·019 | 0·018 |
| 85 | 0·05060 | ,, | 0·032 —0·0345 | 0·0335 |
| 82·5 | 0·04582 | 0·02500 | 0·043 —0·0445 | 0·044 |
| 80 | 0·03102 | ,, | 0·057 —0·060 | 0·058 |
| 75 | 0·03148 | 0·02222 | 0·0855—0·089 | 0·0875 |
| 70 | 0·03372 | 0·01666 | 0·12 —0·13 | 0·125 |
| 65 | 0·03551 | ,, | 0·16 —0·165 | 0·161 |
| 62·75 | 0·02082 | 0·01333 | 0·175 —0·185 | 0·18 |
| 60 | 0·02205 | ,, | 0·235 —0·245 | 0·24 |
| 55 | 0·02244 | ,, | 0·315 —0·325 | 0·32 |
| 50 | 0·01632 | 0·00833 | 0·415 —0·435 | 0·425 |
| 45 | 0·01651 | ,, | 0·58 —0·62 | 0·61 |
| 42·5 | 0·01686 | ,, | 0·705 —0·745 | 0·725 |
| 40 | 0·01682 | ,, | 0·795 —0·82 | 0·815 |
| 35 | 0·01238 | 0·00583 | 1·35 —1·45 | 1·40 |
| 32·8 | 0·01227 | ,, | 1·60 —1·70 | 1·65 |
| 30 | 0·01240 | ,, | 1·76 —1·85 | 1·83 |

## TABLE VII.

Barium hydroxide and methyl *n*-butyrate.

| % alcohol. | $c_{Ba(OH)_2}$. | $c_{ester}$. | Limit *k*. | *k*. |
|---|---|---|---|---|
| 90 | 0·07226 | 0·04444 | 0·055—0·0585 | 0·0565 |
| 85 | 0·07066 | ,, | 0·078—0·082 | 0·081 |
| 82·5 | 0·07301 | 0·03333 | 0·096—0·103 | 0·100 |
| 80 | 0·05288 | ,, | 0·110—0·120 | 0·115 |
| 75 | 0·03495 | 0·02222 | 0·14 —0·16 | 0·150 |
| 70 | 0·03544 | 0·01666 | 0·20 —0·21 | 0·205 |
| 65 | 0·02556 | ,, | 0·275—0·29 | 0·285 |
| 62·75 | 0·02196 | 0·01333 | 0·25 —0·28 | 0·26 |
| 60 | 0·02274 | ,, | 0·31 —0·32 | 0·315 |
| 55 | 0·02167 | ,, | 0·46 —0·485 | 0·47 |
| 50 | 0·01792 | 0·00833 | 0·64 —0·68 | 0·66 |
| 45 | 0·01842 | ,, | 0·795—0·825 | 0·81 |
| 40 | 0·01838 | ,, | 0·985—1·04 | 1·03 |
| 35 | 0·01366 | 0·00583 | 1·95 —2·05 | 2·00 |
| 32·8 | 0·01256 | ,, | 2·15 —2·30 | 2·20 |
| 30 | 0·01302 | ,, | 2·45 —2·65 | 2·55 |

## TABLE VIII.

Barium hydroxide and methyl *o*-chlorobenzoate.

| % alcohol. | $c_{Ba(OH)_2}$. | $c_{ester}$. | Limit *k*. | *k*. |
|---|---|---|---|---|
| 90 | 0·07226 | 0·04444 | 0·098—0·101 | 0·100 |
| 85 | 0·07066 | ,, | 0·131—0·135 | 0·133 |
| 82·5 | 0·07301 | 0·03333 | 0·150—0·160 | 0·155 |
| 80 | 0·05288 | ,, | 0·160—0·170 | 0·166 |
| 75 | 0·03978 | 0·02222 | 0·195—0·205 | 0·203 |
| 70 | 0·03544 | 0·01666 | 0·225—0·245 | 0·235 |
| 62·75 | 0·02196 | 0·01333 | 0·24 —0·26 | 0·255 |
| 60 | 0·02274 | ,, | 0·31 —0·335 | 0·32 |
| 55 | 0·02167 | ,, | 0·43 —0·47 | 0·445 |
| 50 | 0·01792 | 0·00833 | 0·59 —0·63 | 0·61 |
| 45 | 0·01842 | ,, | 0·72 —0·75 | 0·745 |
| 40 | 0·01838 | ,, | 0·95 —0·99 | 0·96 |
| 36·5 | 0·01308 | 0·00583 | 1·49 —1·59 | 1·52 |
| 35 | 0·01366 | ,, | 1·65 —1·85 | 1·70 |
| 32·8 | 0·01256 | ,, | 1·86 —1·99 | 1·93 |
| 30 | 0·01302 | ,, | 2·25 —2·45 | 2·35 |

The solubility of barium hydroxide in solvents rich in alcohol was found to be such that it was not necessary to heat the solvent and base as in the case of ethyl alcohol. The titrations with barium hydroxide were carried out in an atmosphere of hydrogen to prevent the absorption of carbon dioxide.

The authors wish to express their thanks to the Government Grant Committee of the Royal Society for funds placed at their disposal which have defrayed the cost of this research. One of them (W. I. J.) begs to express his thanks to the Master and Fellows of Gonville and Caius College for a scholarship which has enabled him to collaborate in this work.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, August 14th*, 1924.]

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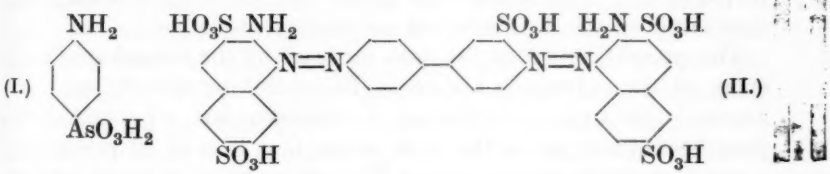
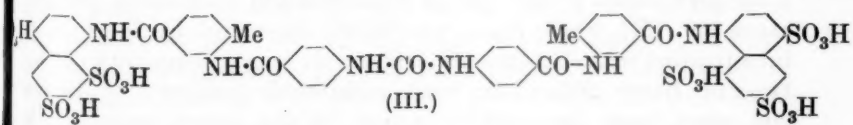
## CCCLV.—*Trypanocidal Action and Chemical Constitution. Part I. Arylamides of* p-*Aminophenylarsinic Acid.*

By HAROLD KING and WILLIAM OWEN MURCH.

THE modern study of chemotherapy is based on the artificial infection of experimental animals and the systematic study of the effect of drugs on the course of the disease produced. Experimental trypanosomiasis in laboratory animals is known to be influenced more or less favourably by various classes of drugs, prominent among which are (1) arsenic compounds, such as derivatives of *p*-aminophenylarsinic acid (I), (2) the azo-dyes of the type of trypan-red (II), and (3) the complex carbamides of the type of Bayer 205 and of preparation 309 (III) of Fourneau and his co-workers.




Each of the substances pictured is a member of a group of similarly constituted substances, all of which exhibit to a greater

or lesser degree trypanocidal action. This specificity is a group property and the aim of investigators has been to prepare in any one group a member in which the trypanocidal action reaches a maximum. As a measure of trypanocidal activity Ehrlich introduced the chemotherapeutic index, I, which is the ratio of the minimum dose, *C*, which will cure a standard infection in an animal without relapse, to the maximum dose, *T*, tolerated by a healthy animal. The primary object, therefore, is to devise a substance in which the curative dose, *C*, is but a minute fraction of the tolerated dose, *T*. The peaks of activity hitherto attained are an index of 1/58 for salvarsan in the treatment of fowl spirillosis, an index of 1/160 for Bayer 205 and a similar value for Fourneau's preparation 309, on experimental trypanosomiasis in small animals. These are exceptional, for Ehrlich expressed the view that we shall "have to be satisfied if we can succeed in obtaining good therapeutic results with the tenth or even fifth or sixth portion of the *dosis tolerata*."

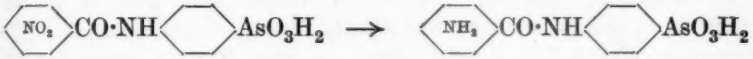
In spite of the extensive researches which have been carried out on the relation between physiological action and chemical constitution, very little has emerged which can be formulated in the way of rules. One generalisation, tacitly accepted by investigators, is that similarity of molecular build, arrangement or structure, and hence similarity of localisation in the living tissues determines similarity of physiological action. Although this statement has a general validity, the converse does not hold; dissimilarity of molecular build does not necessarily preclude similarity of physiological action. These rough generalisations are embodied in the group specificity of the four types of trypanocidal agents mentioned above. There are no safe guides known which will lead to the synthesis of substances of maximal trypanocidal activity within a given group. The discovery of such substances as salvarsan, tryparsamide, trypan-blue, and Bayer 205, although resulting from systematic search, has involved an element of chance.

The present investigation was inspired by the remarkable properties of the substance known as Bayer 205 or latterly as "germanin." Its exact constitution is unknown, but a perusal of the patent specifications in this field shows that it is in all probability a complex amide of the type of Fourneau and co-workers' preparation 309 (III), which latter was indeed discovered by the French investigators in an attempt to prepare an active compound of the type of Bayer 205. The most remarkable property of Bayer 205 apart from its curative action, is the period over which it remains active in the animal body. The case of a rabbit is recorded which after an injection of Bayer 205 remained for five

months protected against repeated injections of *Trypanosoma equiperdum*.

An inspection of the formulæ of trypan-red (II), and Fourneau's preparation 309 (III) reveals a naphthylaminesulphonic acid nucleus duplicated by the attachment of a link. In the azo-dyes both the link and the naphthylaminesulphonic acid can be modified in numerous ways with retention of some trypanocidal activity (Nicolle and Mesnil, *Ann. Inst. Pasteur*, 1906, **20**, 417) and the same applies to the Bayer series (Bayer patents and Fourneau, Tréfouel, and Vallée, *Ann. Inst. Pasteur*, 1924, **38**, 81). The structure which remains uniformly common to the two series is a sulphonated naphthylamine. Inasmuch as the structure $PhAsO_3H_2$ is at the basis of practically all arsenical trypanocidal agents, it was thought that it would be worth while to investigate the effect of attaching to such a nucleus a chain of the type used as a link in the Bayer series. It was hoped that an arsenical of such complexity and containing a type of linking (amide) characteristic of proteins, would remain in the tissues for long periods and exert its action continuously over those periods and not be rapidly excreted as is the case with salvarsan and its allies.

The synthesis of such substances has now been effected. From *p*-aminophenylarsinic acid (I) the three possible o′-, m′-, and p′-*mononitrobenzoyl*-p-*aminophenylarsinic acids* have been prepared and from these the corresponding o′-, m′-, and p′-*aminobenzoyl*-p-*aminophenylarsinic acids* in yields of 60 to 85% of theory.




*p′*-Aminobenzoyl-*p*-aminophenylarsinic acid could not be obtained pure by reduction of the nitro-compound with ferrous chloride and only after much labour by using sodium hyposulphite. The difficulty lies in the separation of the amino-acid from nitro- or partially reduced nitrogen-compounds, as all the salts of the amino-acid with mineral acids are very sparingly soluble, a solubility comparable with that of the by-products. It was, however, readily obtained pure by making use of a reaction mentioned, without any details, by Fourneau, Navarro-Martin, and M. and Mme. Tréfouel (*Ann. Inst. Pasteur*, 1923, **37**, 551) for the preparation of the same compound. In fact, we had this amino-acid in hand when Fourneau's paper appeared. We have now worked out the details of the process mentioned by Fourneau. *p*-Aminobenzoic acid reacts with ethyl chloroformate in presence of sodium hydroxide with production of p-*carbethoxyaminobenzoic acid*. When suspended in acetyl chloride, this acid reacts with phosphorus pentachloride with

production of *carbethoxyaminobenzoyl chloride*. Using ether as a solvent, this aryl radical can be introduced into *p*-aminophenylarsinic acid, in presence of sodium acetate and with addition of sufficient caustic alkali at intervals to keep the reaction faintly alkaline to phenolphthalein, with production of p'-*carbethoxyaminobenzoyl*-p-*aminophenylarsinic acid* (IV).

(IV.) $EtO_2C{\cdot}NH\langle\rangle CO{\cdot}NH\langle\rangle AsO_3H_2$

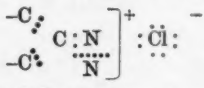
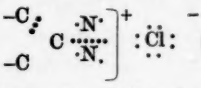
On boiling this urethane with sodium hydroxide, it is converted in 80% yield into *p'*-aminobenzoyl-*p*-aminophenylarsinic acid, an interesting substance which forms a diazonium chloride * sparingly soluble in water. Carbethoxyaminobenzoyl chloride proves to be an excellent reagent for the identification of alcohols, as the *methyl*, *ethyl*, and n-*butyl* esters are solids melting 50 to 70° higher than the corresponding *p*-nitrobenzoyl esters. Experiments are in progress for the introduction of this aryl radical into various alkamines with a view to the production of a series of local anæsthetics.

The maximum dose tolerated by mice, expressed in milligrams per gram of mouse, of this group of six related compounds in comparison with the parent substance, *p*-benzoylaminophenylarsinic acid, is shown below.

| | Bz. | *o'*-$NO_2$. | *m'*-$NO_2$. | *p'*-$NO_2$. | *o'*-$NH_2$. | *m'*-$NH_2$ | *p'*-$NH_2$. |
|---|---|---|---|---|---|---|---|
| *Dosis tolerata* ... | 0·05 | 1·0 | 0·6 | 0·3 | 0·5 | 0·6 | 0·175 |

In describing the curative action, three cases can be distinguished; a substance may not affect, visibly, the number of trypanosomes circulating in the blood stream; it may cause a temporary disappearance of trypanosomes followed by a relapse; or it may bring about a complete cure. The nitro-compounds examined had no action on *T. equiperdum* in mice, whilst the three amino-compounds were non-curative but caused a temporary disappearance of trypanosomes on the following doses: *o'*-$NH_2$ 0·4;

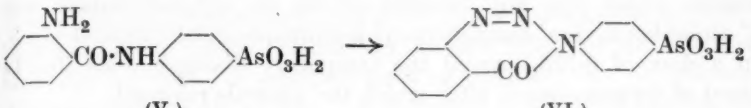
* The introduction of electronic formulæ for organic compounds, two electrons to replace a single bond, has undoubtedly led to a truer picture of many substances. It is of interest that when applied to diazonium salts a new representation is possible which brings out the salient properties, namely, their analogy with ammonium salts and the ease with which they lose nitrogen, in a way not exhibited by any of the older formulæ. Thus Blomstrand's formula would be written electronically thus, (I), but the symmetrical formula

(I.)  (II.) 

(II), in which the nitrogen atoms are attached to the nucleus by single electrons seems to fit the facts better.

*m'*-$NH_2$ 0·18; *p'*-$NH_2$ 0·09. In relation to the tolerated doses the *m*-compound has the most favourable action. Fourneau and co-workers record an index, $C/T = 1/3$, for the para-compound when tested on *T. brucei* in mice.

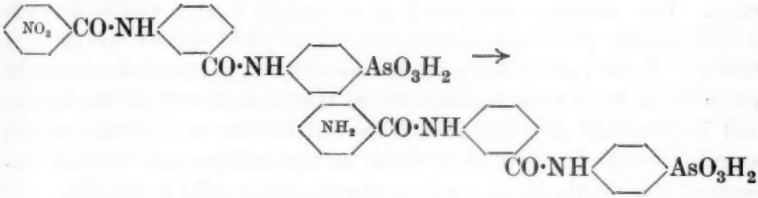
On diazotisation, *o'*-aminobenzoyl-*p*-aminophenylarsinic acid (V) passes instantaneously into the sparingly soluble 1 : 2 : 3-*benztriazone*-3-*phenyl*-p-*arsinic acid* (VI).



(V.) (VI.)

This substance is completely devoid of curative action even on the maximal tolerated dose, 0·025.

By a repetition of the process of nitro-benzoylation, the o''-, m''-, and p''-*mononitrobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acids* and the o''-, m''-, and p''-*mononitrobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acids* have been prepared. On reduction, they are converted into the corresponding o''-, m''-, and p''-*aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acids* and o''-, m''-, and p''-*aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acids* respectively. Thus, for example :



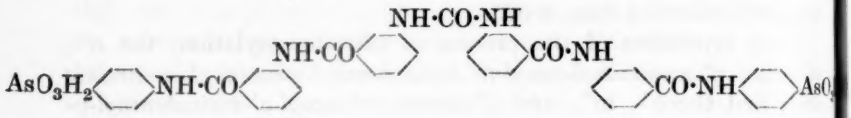
The separation of these trinuclear amino-acids from partly reduced by-products, which are always formed when ferrous chloride is used, proved a very difficult problem, but was eventually solved by making use of the solvent action, on the amino-acids, of *N*- or 2*N*-nitric acid, free from nitrous acid, at a temperature of 50°. Relatively large volumes of acid are required, but on addition of saturated sodium acetate solution these complex arsinic acids are usually precipitated in a crystalline condition. The yields average 50 to 80% in the case of the *m*-amino-derivatives and 30 to 50% in the case of the *o*- and *p*-derivatives. All these amino-arsinic acids are retained with persistence by the ferric hydroxide precipitate and are effectively removed only by repeated extraction with 0·4*N*-alkali. The most striking feature of these acids is the slight solubility of their salts with mineral acids and with a mole-

cular proportion of alkali-metal hydroxides. Their maximal tolerated doses are shown below.

| | *o''*-$NO_2$*m'p.* | *m''*-$NO_2$*m'p.* | *p''*-$NO_2$*m'p.* | *o''*-$NH_2$*m'p.* | *m''*-$NH_2$*m'p.* | *p''*-$NH_2$*m'p.* |
|---|---|---|---|---|---|---|
| *T* | 0·3 | 0·1 | 0·04 | 0·4 | 0·1 | 0·25 |
| | *o''*-$NO_2$*o'p.* | *m''*-$NO_2$*o'p.* | *p''*-$NO_2$*o'p.* | *o''*-$NH_2$*o'p.* | *m''*-$NH_2$*o'p.* | *p''*-$NH_2$*o'p* |
| *T* | 0·4 | 0·1 | 0·1 | 0·1 | 0·1 | 0·05 |

The only amino-compound of these six isomeric trinuclear compounds which had any curative action on trypanosomiasis was *p''*-aminobenzoyl-*m'*-aminobenzoyl-*p*-aminophenylarsinic acid which, on a dose of 0·175, caused the temporary disappearance (for 14 days) of trypanosomes, after which the animals relapsed.

The ultimate aim of this investigation was the production of carbamides of the type:




Although *p*-aminophenylarsinic acid, when treated with carbonyl chloride in toluene in presence of sodium acetate, gives a 93% yield of *s*-diphenylcarbamide-*pp'*-diarsinic acid, yet under the same conditions or even using excess of carbonyl chloride, the *p*-amino-compounds of the trinuclear series give no carbamide or only a trace. The *o*-amino-compounds give slightly better yields, but the *m*-compounds give the carbamides in a yield of 60 to 70% of theory. In the case of the *p*-compounds this apparent non-reactivity seems to be due to the insolubility of the sodium salt of the amino-acid in presence of sodium acetate, but in the case of the *o*-compounds the effect is probably steric, as the sodium salt of *o''*-aminobenzoyl-*o'*-aminobenzoyl-*p*-aminophenylarsinic acid is soluble.

These carbamides have a molecular weight of 936 and are the most complex colourless compounds of arsenic of known molecular weight. They exhibit marked colloidal properties, a 1% solution of the sodium salt of the s-*carbamide* of m''-*aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acid*, for instance, setting to a gel on keeping for 24 hours. Unfortunately, they are totally devoid of any action on trypanosomes. If this striking result be compared with the trypanocidal action of the members of the Bayer series (Fourneau *et alii*, *loc. cit.*), one cannot but contrast the physical properties of the two series and observe the accumulation of sulphonic acid groups conferring solubility on the members of the Bayer series (Bayer 205, a sodium salt, is extremely soluble in water) with the sparing solubility of these complex arsinic acids, one of their most salient features. The interesting results already

obtained in development of this idea will be embodied in a future communication.

In connexion with the use of ferrous chloride and caustic alkali for the reduction of nitro-arsinic acids, first used for this purpose by Benda (*Ber.*, 1901, **44**, 3302) and later strongly recommended by Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1580), we have repeatedly noticed a curious variation in the yield of amino-acids depending on the way the reagents are mixed. If *m'*-nitrobenzoyl-*p*-aminophenylarsinic acid be dissolved in caustic alkali and then ferrous chloride and caustic alkali be added simultaneously so that the reaction remains definitely on the alkaline side, the yield is ab ut 40%; if, however, the ferrous chloride be added completely and then the additional alkali quite separately, the yield is raised to 85%.

For the characterisation of arsinic acids, melting-point determinations have proved of little value owing to their indefiniteness. We have found that the reaction of ammoniacal solutions of the arsinic acids with lithium, magnesium, calcium, and barium chlorides, in the first place at room temperature and then on warming, when carried out with solutions of definite strength, forms a very valuable means of identifying arsinic acids. There may be immediate precipitation, or only on heating, and, in addition, the crystalline character of the precipitated salts may be very diverse.

We are extremely indebted to Miss F. M. Durham and Miss J. Marchal of this department for the painstaking care with which they have determined the toxicities and trypanocidal activities of the compounds described in this paper, without which the results would have been of far inferior interest.

## Experimental.

*Benzoyl*-p-*aminophenylarsinic Acid.*—To a vigorously stirred solution, at 0°, of sodium *p*-aminophenylarsinate (25 g. of hydrated salt) in 250 c.c. of water and 150 c.c. of 10% sodium hydroxide, benzoyl chloride (2 mols.) was slowly added. After acidification, the mixed acids were collected, dissolved in 2*N*-ammonia, and the magnesium salt of the required acid precipitated by adding magnesium chloride and heating on the water-bath. The magnesium salt was decomposed by acid and gave 21·2 g. of benzoyl-*p*-aminophenylarsinic acid.

This acid, briefly mentioned in D.R.-P. 191548, crystallises from glacial acetic acid or formic acid, in which it is very sparingly soluble, in small prisms (Found : As = 23·3. $C_{13}H_{12}O_4NAs$ requires As = 23·3%). It forms a sparingly soluble *ammonium* salt which

crystallises in hydrated long needles (Found: Loss on air-dried salt=8·9; in dried salt, ammonium N=4·1. $C_{13}H_{11}O_4NAsNH_4,2H_2O$ requires $2H_2O = 9·6\%$; anhydrous salt requires ammonium N = 4·1%).

p'-*Nitrobenzoyl*-p-*aminophenylarsinic acid* was prepared in a similar manner to the foregoing, except that the *p*-nitrobenzoyl chloride was added dissolved in benzene. The nitro-acid was isolated *via* the magnesium salt. It dissolves very sparingly in boiling glacial acetic acid, somewhat more readily in boiling formic acid, and separates in clusters of fine needles. It is unexpectedly much more soluble in boiling alcohol than the unsubstituted benzoyl-*p*-aminophenylarsinic acid (Found: As = 20·3. $C_{13}H_{11}O_6N_2As$ requires As = 20·5%). The *sodium* and *ammonium* salts are sparingly soluble and crystallise in needles.

m'-*Nitrobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same way as the *p'*-nitro-acid. It crystallises from boiling glacial acetic or formic acid, in which it is very sparingly soluble, in long needles (Found: As = 20·2. $C_{13}H_{11}O_6N_2As$ requires As = 20·5%). The mono-*sodium* and *ammonium* salts are sparingly soluble in water and crystallise in needles.

o'-*Nitrobenzoyl*-p-*aminophenylarsinic acid* was prepared similarly to the foregoing acids, but was isolated by extracting the crude dried mixture of *o*-nitrobenzoic and *o'*-nitrobenzoyl-*p*-aminophenylarsinic acids with ether in a Soxhlet extractor to remove the *o*-nitrobenzoic acid. The arsinic acid separates from boiling water in needles, from cold alcohol in plates, and crystallises well from glacial acetic or formic acid (Found: As = 20·4. $C_{13}H_{11}O_6N_2As$ requires As = 20·5%).

p-*Carbethoxyaminobenzoic Acid.*—*p*-Aminobenzoic acid hydrochloride (1 mol.) was dissolved in *N*-sodium hydroxide (2 mols.), chilled below 0°, and shaken vigorously with four successive portions of ethyl chloroformate (1·1 mols.) for 15 minutes. The solid was collected, suspended in *N*-hydrochloric acid, filtered, and washed with water. The yield was almost quantitative. This acid, m. p. 208—209° (corr.), is soluble in 5 parts of boiling spirit and crystallises in clusters of bold needles. It is readily soluble in ethyl acetate, acetic acid, or methyl ethyl ketone, sparingly soluble in hot benzene or chloroform, and somewhat more readily soluble in warm ether (Found: C = 57·1; H = 5·3. $C_{10}H_{11}O_4N$ requires C = 57·4; H = 5·3%). p-*Carbethoxyaminobenzoyl chloride* is prepared from the dried acid by treating with freshly distilled acetyl chloride (5 vols.) followed by phosphorus pentachloride (1 mol.). The reaction takes place immediately and is finished by warming. On again cooling, the acid chloride crystal-

lises out in fine needles. It is soluble in ten parts of ether. For use in benzoylation experiments the solvents are removed under reduced pressure below 50° and the product freed from traces of impurities by evaporating to dryness once or twice with dry ether. *Methyl* p-*carbethoxyaminobenzoate*, m. p. 161—162° (corr.), crystallises out straightway in diamond- or envelope-shaped plates when the acid chloride is treated with a small volume of methyl alcohol (Found: C = 59·0; H = 5·8. $C_{11}H_{13}O_4N$ requires C = 59·2; H = 5·9%).

The *ethyl* ester, prepared similarly, crystallises in rosettes of flat needles, m. p. 131—132° (corr.). The n-*butyl* ester crystallises from ethyl alcohol in glistening needles, m. p. 89—90° (corr.). n-*Butyl* p-*nitrobenzoate* was prepared for comparison with the preceding. It melts at 35—36° (corr.), and is best recrystallised from a small volume of ethyl alcohol by cooling to 0°. It is very soluble in organic solvents and crystallises in filmy needles.

p′-*Aminobenzoyl*-p-*aminophenylarsinic Acid*.—To a solution of *p*′-nitrobenzoyl-*p*-aminophenylarsinic acid [14·6 g. in 43 c.c. of 2*N*-sodium hydroxide (2 mols.) and 80 c.c. of water], cooled below 0°, freshly standardised sodium hyposulphite (3 mols.) was added in four equal portions (28 g. in all); throughout, the temperature must be kept below 2° to ensure good yields. The mixture of amino-acid and unchanged nitro-compound which separated, was dissolved in 0·5*N*-ammonia, the solution was filtered, and neutralised (congo-paper) with concentrated hydrochloric acid. The precipitated acids, after filtration, while still damp, were thoroughly ground up with 100 c.c. of 40% sulphuric acid (by weight). After filtration, the solid undissolved was re-extracted with further small portions of 40% acid so long as any diazotisable material was left undissolved. Usually about another 50 c.c. were required. The combined filtrates were poured into water and the hydrolysed base was collected and washed free from sulphate by 6% acetic acid (yield about 70%). The properties of the pure material are described below.

p′-*Carbethoxyaminobenzoyl*-p-*aminophenylarsinic Acid*.—*p*-Aminophenylarsinic acid (2·7 g.) was dissolved in 25 c.c. of water with addition of 6·5 c.c. of 2*N*-sodium hydroxide (1 mol.) and 25 c.c. of saturated sodium acetate solution. The solution was made faintly alkaline to phenolphthalein ($p_H$ = 8·5) by addition of 3 c.c. of 2*N*-sodium hydroxide. *p*-Carbethoxyaminobenzoyl chloride (2 mols.), dissolved in 50 c.c. of dry ether, was added all at once and the mixture shaken for 30 minutes. The alkalinity to phenolphthalein was again restored by addition of 29 c.c. of 2*N*-sodium hydroxide, and shaking continued. This process was continued so

long as phenolphthalein was decolorised. In all, 37 c.c. of 2*N*-sodium hydroxide were required to produce permanent alkalinity to phenolphthalein. The ether was removed under reduced pressure and the solution made acid to congo-paper. The precipitated solid was dried and extracted with ether, the insoluble solid consisting of the required arsinic acid in 50% yield. This acid is almost insoluble in the usual organic solvents, but crystallises from boiling 90% formic acid, in which it is very sparingly soluble, in minute needles (Found: As = 18·1. $C_{16}H_{17}O_6N_2As$ requires As = 18·4%).

*Partial Hydrolysis of* p′-*Carbethoxyaminobenzoyl*-p-*aminophenylarsinic Acid.*—A solution of the urethane (10 g.) in 100 c.c. (4 mols.) of *N*-sodium hydroxide was boiled for 5 minutes, diluted with 150 c.c. of water, cooled, and concentrated hydrochloric acid added with vigorous stirring until the reaction was just neutral to litmus. A permanent crystalline precipitate was thus obtained of sodium *p*′-aminobenzoyl-*p*-aminophenylarsinate (yield about 80%). Further quantities could be obtained by making the filtrate neutral to congo-paper, repeating the hydrolytic process on the precipitated solid, and isolating the pure amino-acid as the mono-sodium salt as before. The free acid was obtained by rendering a suspension of the sodium salt in water neutral to congo-paper. p′-*Aminobenzoyl*-p-*aminophenylarsinic acid* thus prepared is a white powder soluble in dilute ammonia, forming a colourless solution, but when prepared by reduction of the nitro-compound it always retains traces of impurities which give a yellow colour in alkaline solution. It is very readily soluble in cold 90% formic acid and may be recrystallised from more aqueous formic acid in small quantities, separating in leaflets. It is very sparingly soluble in boiling 25% formic acid or glacial acetic acid (Found: As = 22·1. $C_{13}H_{13}O_4N_2As$ requires As = 22·3%). It is feebly basic, but forms crystalline salts readily by trituration of the free base with a little water followed by addition of concentrated acids. Under such conditions, the *hydrochloride* (Found: Cl = 9·8. $C_{13}H_{13}O_4N_2As,HCl$ requires Cl = 9·5%), *hydrobromide*, and *nitrate* separate straightway, but the *phosphate*, *sulphate*, and *perchlorate* only tardily. The base diazotises in *N*-hydrochloric acid, forming a clear yellow solution which deposits a *diazonium chloride* crystallising in pale yellow needles from moderately concentrated solutions. When added to alkaline β-naphthol, a crimson-red soluble azo-compound is formed. The *mono-ammonium* salt is readily obtained, crystallising in hexagonal plates, by allowing an ammoniacal solution to stand exposed to the air (Found: ammonium N = 4·0. $C_{13}H_{12}O_4N_2AsNH_4$ requires ammonium N = 4·0%).

m′-*Aminobenzoyl*-p-*aminophenylarsinic Acid.*—(a) *Reduction with hyposulphite.* m′-Aminobenzoyl-*p*-aminophenylarsinic acid can be obtained by reduction of the corresponding nitro-compound with sodium hyposulphite, but only in a very poor yield. This appears to be due to its solubility in the sulphite liquors and to the simultaneous formation of sulphonic acids. These could be isolated as a mixture of acids by precipitating as the magnesium salt from hot ammoniacal solution. Their formation is paralleled by the formation of mono- and di-sulphonic acids of *m*-aminobenzoic acid by reduction of nitrobenzoic acid by sulphite (Walther, D.R.-P. 109487).

(b) *Reduction with ferrous chloride.* To a solution of the nitro-compound (22 g.) in 2*N*-sodium hydroxide (220 c.c., cooled to 0°), were added, with vigorous stirring, 73 g. of ferrous chloride (10% excess) in 100 c.c. of water and finally 250 c.c. of 2*N*-sodium hydroxide. The temperature throughout was kept below 0°. The ferric hydroxide was filtered off and extracted twice with 250 c.c., each time, of 0·4*N*-sodium hydroxide. The combined filtrates, made neutral to congo, deposited the amino-acid mixed with partly reduced products. The amino-acid was extracted by *N*-hydrochloric acid so long as diazotisable material was left and precipitated by removing the acidity to congo-paper by addition of saturated sodium acetate solution. The yield averages 15·3 g. m′-*Aminobenzoyl*-p-*aminophenylarsinic acid* crystallises as a felt of minute needles. It is readily soluble in dilute acids and on evaporation to a small volume, the hydrochloride crystallises (Found : As = 22·2. $C_{13}H_{13}O_4N_2As$ requires As = 22·3%).

o′-*Aminobenzoyl*-p-*aminophenylarsinic Acid.*—The reduction of the *o*′-nitro-compound was carried out as in the preceding, but the acid was isolated as follows. The combined filtrates from the ferric hydroxide were neutralised to congo-paper, and the portion precipitated collected. This was warmed to 50° with 75 c.c. of *N*-nitric acid (freed from nitrous acid by a current of dust-free air), which dissolved the major portion of the base. On filtration and addition of saturated sodium acetate, the *o*′-amino-acid separated in glistening leaflets (yield 9·2 g.). A further quantity was isolated from the first precipitation mother-liquors by adding ammonia and magnesium chloride and heating on the water-bath. The magnesium salt was dissolved in *N*-hydrochloric acid (60 c.c.), and the free amino-acid precipitated by addition of saturated sodium acetate. This gave an additional 2·2 g. This arsinic acid forms very sparingly soluble, crystalline salts with hydrochloric and sulphuric acids. It is readily soluble in 3*N*-nitric acid, but, on keeping, a beautifully crystalline nitrate separates in long

prisms. When diazotised, it does not as a rule couple with alkaline β-naphthol, as its conversion into 1 : 2 : 3-benztriazone-3-phenyl-*p*-arsinic acid is too rapid. On occasions, this transformation appeared to be retarded by unknown factors and coupling ensued with production of a blood-red colour (Found: As = 22·1. $C_{13}H_{13}O_4N_2As$ requires As = 22·3%).

1 : 2 : 3-*Benztriazone*-3-*phenyl*-p-*arsinic Acid*.—*o'*-Aminobenzoyl-*p*-aminophenylarsinic acid (1·0 g.) was added to 10 c.c of *N*-nitric acid, when a crystalline nitrate separated. Sodium nitrite (about 1·5 mols.) in water was added at 0°, when the whole of the nitrate slowly passed into solution, the needles of the salt being replaced by microcrystalline leaflets of the triazone. The yield was quantitative. This arsinic acid is insoluble in dilute acids. It is practically insoluble in boiling acetic acid, but crystallises from boiling 90% formic acid in diamond-shaped plates (Found: As = 21·3. $C_{13}H_{10}O_4N_3As$ requires As = 21·6%).

p''-*Nitrobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared similarly to the previously described nitrobenzoyl compounds. Free *p*-nitrobenzoic acid was removed by ether extraction, and any *m'*-aminobenzoyl-*p*-aminophenylarsinic acid by trituration with 3*N*-hydrochloric acid. The yield was 12 g. from 10·1 g. of amino-acid. It is soluble in 0·2*N*-ammonia and, on standing, the *ammonium* salt crystallises in glistening plates (Found: ammonium N = 2·7; As = 14·6. $C_{20}H_{19}O_7N_4As$ requires ammonium N = 2·8; As = 14·9%).

m''-*Nitrobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same manner as the preceding. It has a tendency to separate as an oil on acidification of alkaline solutions, but rapidly solidifies when acidity to congo is reached. The yield was 13·2 g. from 10·1 g. of *m'*-amino-compound. This arsinic acid is soluble in 2*N*-sodium hydroxide without colour development. It is soluble in 100 parts of boiling 85% formic acid and crystallises, on cooling, in plates. The ammonium salt, unlike that of the *p*-derivative, is very soluble in water (Found: As = 15·5. $C_{20}H_{16}O_7N_3As$ requires As = 15·4%).

o''-*Nitrobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same way as the two preceding. Admixed *o*-nitrobenzoic acid was removed by stirring the mixed acids with hot water. The insoluble acid was the required acid and weighed 15·1 g. (from 10·1 g. of the *m'*-amino-acid). As prepared above, the acid is amorphous, but crystallises from 85% formic acid in bold plates containing water of crystallisation (Found: loss = 4·1, 5·1. $1\frac{1}{2}H_2O$ requires 5·3% loss. Found: on dried material, As = 15·1. $C_{20}H_{16}O_7N_3As$ requires As = 15·5%). It also crystal-

lises from this solvent as a dihydrate in needles (Found : $H_2O$ = 6·9. $2H_2O$ requires 6·9%). It is very sparingly soluble in glacial acetic acid. The ammonium salt separates in microscopic needles and is very sparingly soluble in water, once it has separated.

p''-*Aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic Acid.*—*p*''-Nitrobenzoyl-*m*'-aminobenzoyl-*p*-aminophenylarsinic acid (9·7 g.), dissolved in 73 c.c. of 2*N*-sodium hydroxide at − 5°, was treated slowly with 24 g. (10% excess) of ferrous chloride in 34 c.c. of water, and finally 83 c.c. of 2*N*-sodium hydroxide were run in. The ferric hydroxide after filtration was thoroughly re-extracted thrice with 83 c.c. of 0·4*N*-sodium hydroxide, each time. The combined filtrates were neutralised to congo-paper and the collected solids, when washed, were made into a thin cream with water and added to 4000 c.c. of 2*N*-nitric acid (free from nitrous acid), kept vigorously stirred at 50°. The turbid solution was rapidly filtered, refiltered after addition of charcoal, and the acidity to congo-paper removed by addition of saturated sodium acetate solution. The free amino-acid separated straightway as a microcrystalline, white powder (yield about 4·5 g.). Further small quantities can be obtained, if necessary, by taking the solid undissolved by the warm nitric acid, regenerating the base through ammonia solution, and repeating the above process so long as diazotisable material is present. This acid forms a series of crystalline salts with hydrochloric, sulphuric, and nitric acids which are extremely insoluble in water but undergo hydrolysis readily. The acid diazotises and couples with alkaline β-naphthol with production of a deep red solution (Found : As = 16·6. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%).

m''-*Aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic Acid.*—The nitro-acid (9·7 g.) was reduced in the same way as the preceding. The total precipitate obtained on acidifying the alkaline extracts of the ferric hydroxide was made into a cream with water and added to 2500 c.c. of *N*-nitric acid at 50°, and the free amino-acid isolated as before (yield about 8 g.). This acid, so prepared, crystallises in leaflets (Found : As = 16·3. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%). The salts with mineral acids are very sparingly soluble, the sulphate crystallising in leaflets, the hydrochloride in needles, and the nitrate in balls of silky needles. It diazotises best in nitric acid solution and couples with β-naphthol with a deep-red colour. The ammonium salt crystallises in fine needles and is rather sparingly soluble in water.

o''-*Aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same way as the preceding, except that 960 c.c. of *N*-nitric acid were sufficient to dissolve the amino-acid (yield only 3·25 g.). This arsinic acid crystallises, when liberated from dilute

acid solutions by sodium acetate, in fine needles (Found: As = 16·7. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%). It is not soluble in 3*N*-mineral acids, but dissolves on adding more concentrated acids. The sulphate, nitrate, and hydrochloride crystallise in microscopic needles. On diazotisation, it very rapidly passes into the insoluble, presumably 1 : 2 : 3-benztriazone-3-*m'*-benzoyl-*p*-aminophenylarsinic acid, but if poured immediately after diazotisation into alkaline β-naphthol it couples weakly.

p''-*Nitrobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid*, prepared similarly to the three preceding nitro-acids (yield 11·5 g.), crystallises from 37 parts of boiling 90% formic acid in short needles (Found: As = 15·2. $C_{20}H_{16}O_7N_3As$ requires As = 15·5%).

m''-*Nitrobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid*, prepared in the same way as the preceding (yield 11·5 g.), crystallises from 25 volumes of 90% formic acid in rhombic-shaped leaflets. It is very much less soluble in acetic acid. Its solution in ammonia is colourless and when allowed to evaporate in the air gives rise to a gel which, on further drying, yields an ammonium salt crystallising in fine, silky needles (Found: As = 15·3. $C_{20}H_{16}O_7N_3As$ requires As = 15·5%).

o''-*Nitrobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid*, prepared in the same way as the preceding, is best purified by adding it to 40 volumes of hot water and collecting the undissolved solid (yield 12·4 g.). It is converted into a felt of crystals by warming with two volumes of 90% formic acid and crystallises well from this solvent, in which it dissolves to the extent of about 6% at the boiling point, in soft, glistening needles (Found: As = 15·3. $C_{20}H_{16}O_7N_3As$ requires As = 15·5%). The ammonium salt crystallises readily from water in leaflets.

p''-*Aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same way as the three preceding amino-acids of the trinuclear series. Two litres of 2*N*-nitric acid at 50° were sufficient to extract the amino-acid from non-basic impurities. On addition of saturated sodium acetate solution, the amino-arsinic acid separated in a gelatinous condition, but rapidly became transformed into fine needles (yield 4·0 g.). It diazotises with production of a bright yellow colour and couples with alkaline β-naphthol with production of a blood-red solution. The sulphate is sparingly soluble in hot 2*N*-sulphuric acid and crystallises in small needles; the nitrate is soluble in hot 3*N*-nitric acid and separates as an oil on cooling, which eventually crystallises in short rods; the hydrochloride is soluble in hot 3*N*-hydrochloric acid and crystallises in silky needles (Found: As = 16·5. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%).

m''-*Aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid* was

prepared in the same way as the preceding, except that 3 litres of *N*-nitric acid were required to extract the amino-acid (yield 5·0 g.). It diazotises and couples with alkaline β-naphthol with production of a deep cherry-red colour. Its salts with dilute mineral acid are extremely insoluble, but more soluble when heated. The nitrate crystallises in needles, the hydrochloride likewise, and the sulphate in diamond-shaped leaflets. The ammonium salt is also crystalline (Found: As = 16·3. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%).

o''-*Aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic acid* was prepared in the same way as the preceding, save that 2 litres of *N*-nitric acid at 50° were sufficient to extract the amino-acid (yield 3·6 g.). This arsinic acid crystallises in microscopic leaflets. When diazotised and added to alkaline β-naphthol, it does not as a rule couple with formation of a red colour, but under undetermined conditions coupling has been observed. The nitrate and hydrochloride are soluble in warm 3*N*-nitric and hydrochloric acids and crystallise in rosettes of needles. The sulphate is soluble in hot 2*N*-sulphuric acid and crystallises in microscopic needles (Found: As = 16·7. $C_{20}H_{18}O_5N_3As$ requires As = 16·5%).

s-*Diphenylcarbamide*-4 : 4'-*diarsinic Acid*.—This carbamide is briefly mentioned in D.R.-P. 191548. It is obtained in 93% yield by the following process. *p*-Aminophenylarsinic acid (4·3 g.) was neutralised with 10 c.c. of 2*N*-sodium hydroxide and 100 c.c. of half-saturated sodium acetate solution were added. Two successive portions, each 20 c.c., of a 12·5% solution of carbonyl chloride in toluene were added with vigorous shaking. After 30 minutes, the toluene was removed by ether extraction and the aqueous layer made acid to congo-paper. The precipitated acid was obtained free from diazotisable material by washing with 0·5*N*-hydrochloric acid. *s*-Diphenylcarbamide-4 : 4'-diarsinic acid is very sparingly soluble in boiling 90% formic acid and crystallises in microscopic needles (Found: As = 32·7. $C_{13}H_{14}O_7N_2As$ requires As = 32·6%).

*The* s-*Carbamide of* m''-*Aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic Acid*.—The amino-acid (3·55 g.) was dissolved in 50 c.c. of water with the aid of 7·4 c.c. (1·9 mol.) of 2*N*-sodium hydroxide. On addition of 50 c.c. of saturated sodium acetate solution a partial separation of the sodium salt of the amino-arsinic acid occurred. The solution was cooled to 0° and 40 c.c. of a 12·5% solution of carbonyl chloride in toluene were added in 10 c.c. portions with vigorous shaking over a period of 30 minutes. The precipitated product, after being made faintly acid to congo-paper, was collected and washed with water, and ether to remove toluene, and added in the form of a thin cream with water to 1000 c.c. of *N*-nitric acid, kept stirred at 50°. After filtration, the filtrate gave 0·5 g. of unchanged

amino-arsinic acid, on addition of saturated sodium acetate solution, whilst the insoluble gelatinous product on the filter consisted of the required carbamide. It was purified by dissolving in dilute ammonia and adding charcoal. On filtration and acidification, the carbamide was precipitated as a voluminous, gelatinous product which, on keeping 24 hours, could be filtered off and washed free from precipitating ions (yield 2·5 g.). This substituted carbamide has marked colloidal properties [Found: As = 15·7. $(C_{20}H_{17}O_5N_3As)_2CO$ requires As = 16·0%]. The maximum tolerated dose for mice is 0·1 mg. per gram of mouse.

*The* s-*Carbamide of* m''-*Aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic Acid.*—This carbamide was prepared in the same way as the preceding but using 8 mols. of carbonyl chloride (yield 2·65 g. from 4·55 g. of amino-arsinic acid). When dried in a vacuum, it forms a voluminous, amorphous powder. When acid is added to its ammoniacal solution, long before neutrality to congo-paper is reached the solution remains clear but assumes the character of a viscid jelly. As neutrality or faint acidity is reached, the carbamide separates in a flocculent condition. The ammonium salt is gelatinous [Found: As = 15·7. $(C_{20}H_{17}O_5N_3As)_2CO$ require As = 16·0%]. The maximum tolerated dose for mice is 0·025 mg. per gram of mouse.

*Action of Carbonyl Chloride on the* p''-*Aminobenzoyl Derivatives of* m'- *and* o'-*Aminobenzoyl*-p-*aminophenylarsinic Acids.*—Under parallel conditions to the formation of the two carbamides described above, these two arsinic acids gave only traces of the required carbamides. The amino-arsinic acids were recovered unchanged.

*The* s-*Carbamide of* o''-*Aminobenzoyl*-m'-*aminobenzoyl*-p-*aminophenylarsinic Acid.*—Prepared in the same way as those described above, the yield of carbamide was only 0·75 g. from 2·4 g. of arsinic acid. It forms an amorphous powder with marked colloidal properties.

*The* s-*Carbamide of* o''-*Aminobenzoyl*-o'-*aminobenzoyl*-p-*aminophenylarsinic Acid.*—Prepared in the same way as the preceding, the yield was 0·1 g. from 4·55 g. of amino-acid. When liberated from ammoniacal solutions, it separates in a gelatinous condition. Like its isomerides, it exhibits marked colloidal properties.

All the foregoing arsinic acids have been compared under standard conditions as follows: A 1% solution of the acid in 0·2*N*-ammonia (2 c.c.) was treated with 0·1 c.c. of 5% lithium, magnesium, calcium, or barium chloride, first at room temperature and then, if no precipitate appeared within a few minutes, at the temperature of the boiling-water bath. As all the acids are derivatives of *p*-aminophenylarsinic acid, for brevity's sake only the substituting group is denoted

in the abbreviated title, and cold and hot solutions are denoted by c. and h.

| Acid. | Li. | Mg. | Ca. | Ba. |
|---|---|---|---|---|
| Bz | h. ppt. | h. ppt. | c. ppt. | h. hexagonal leaflets changing to silky needles. |
| *p'*-$NO_2$Bz | h. crystalline. | c. ppt. | c. ppt. | h. crystalline. |
| *m'*-$NO_2$Bz | h. clusters of needles. | h. microcrystalline. | c. ppt. | h. leaflets. |
| *o'*-$NO_2$Bz | no ppt. | h. microcrystalline. | h. rosettes of needles. | no ppt. |
| Urethane of *p'*-$NH_2$Bz | c. microcrystalline. | c. amorphous. | c. amorphous. | c. diamond-shaped plates. |
| *p'*-$NH_2$Bz | h. amorphous. | h. amorphous. | c. microcrystalline. | h. long needles. |
| *m'*-$NH_2$Bz | h. ppt. | c. amorphous. | c. amorphous. | h. microcrystalline. |
| *o'*-$NH_2$Bz | h. microcrystalline. | h. microcrystalline. | c. tufts of needles. | h. leaflets. |
| Benztriazone | h. microcrystalline. | c. spheroids. | c. amorphous. | h. prisms. |
| *p''*$NO_2$Bz*m'*$NH_2$Bz | c. microcrystalline. | c. microcrystalline. | c. microcrystalline. | c. microcrystalline. |
| *m''*$NO_2$Bz*m'*$NH_2$Bz | h. microcrystalline. | c. amorphous. | c. amorphous. | c. amorphous; |
| *o''*$NO_2$Bz*m'*$NH_2$Bz | h. spheroids. | c. amorphous. | c. amorphous. | c. spheroids. h. fine needles. |
| *p''*$NH_2$Bz*m'*$NH_2$Bz | h. amorphous. | c. amorphous. | c. amorphous. | h. amorphous. |
| *m''*$NH_2$Bz*m'*$NH_2$Bz | c. spheroids. | c. microcrystals. | c. microcrystals. | h. spheroids. |
| *o''*$NH_2$Bz*m'*$NH_2$Bz | h. spheroids. | c. amorphous. | c. amorphous. | no ppt. |
| *p''*$NO_2$Bz*o'*$NH_2$Bz | no ppt. | c. microscopic needles. | c. microscopic needles. | c. needles. |
| *m''*$NO_2$Bz*o'*$NH_2$Bz | ,, | c. amorphous. h. crystalline. | c. amorphous, later filiform. | c. amorphous. h. crystalline. |
| *o''*$NO_2$Bz*o'*$NH_2$Bz | ,, | c. rosettes. | c. rosettes of leaflets. | c. long silky needles. |
| *p''*$NH_2$Bz*o'*$NH_2$Bz | ,, | c. amorphous. | c. amorphous. | c. plates. h. needles. |
| *m''*$NH_2$Bz*o'*$NH_2$Bz | ,, | c. amorphous. | c. crystalline tufts. | c. amorphous changing to needles. |
| *o''*$NH_2$Bz*o'*$NH_2$Bz | ,, | c. amorphous. | c. amorphous, changing to needles. | no ppt. |
| *s*-Carbamide | ,, | c. tufts of needles. | c. microcrystalline powder. | h. crystalline powder. |
| *s*-Carbamide of *m''*$NH_2$Bz*m'*$NH_2$Bz | c. syrup. h. gelatinous ppt. | c. gelatinous ppt. | c. gelatinous ppt. | c. gelatinous ppt. |
| *s*-Carbamide of *m''*$NH_2$Bz*o'*$NH_2$Bz | h. clear gel. | c. gelatinous ppt. | c. gelatinous ppt. | c. gelatinous ppt. |
| *s*-Carbamide of *o''*$NH_2$Bz*m'*$NH_2$Bz | no ppt. | c. amorphous flocks. | c. amorphous flocks. | c. amorphous flocks. |
| *s*-Carbamide of *o''*$NH_2$Bz*o'*$NH_2$Bz | h. gelatinous ppt. | c. gelatinous ppt. | c. gelatinous ppt. | c. gelatinous ppt. |

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## CCCLVI.—*Isomeric Benzoyl Derivatives from Vinyldiacetonamine.*

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DURING an investigation of the *N*-methyl derivatives of vinyldiacetonamine (Kipping, J., 1923, **123**, 3115) an attempt was made to benzoylate the vinyl base by the Schotten-Baumann method; not

a trace of a benzoyl derivative, except benzoic anhydride, separated from the solution. In consequence of this failure, the action of benzoyl chloride alone on pure vinyldiacetonamine was examined and again unexpected results were observed. A crystalline benzoyl derivative, melting at 156°, was easily obtained under certain conditions, but the yield was generally poor and a considerable proportion of the product consisted of a thick oil.

A resumed study has shown that the compound, m. p. 156°, is doubtless a normal *N*-benzoyl derivative of the vinyl base, which is best obtained by treating the pure base (2 mols.) with benzoyl chloride (1 mol.); the yield, however, calculated from the equation $2C_8H_{15}ON + C_6H_5{\cdot}COCl = C_8H_{14}ON{\cdot}CO{\cdot}C_6H_5 + C_8H_{15}ON,HCl$, is only about 70% of the theoretical. If the proportion of benzoyl chloride is increased, the yield is diminished, and when more than one molecular proportion is used there is obtained a thick oil; from the latter, a benzoyl derivative melting at 110° can be isolated and the remaining oil, on distillation, decomposes entirely, giving benzamide and a liquid which contains benzonitrile. Both benzoyl derivatives have the molecular formula $C_{15}H_{19}O_2N$ and appear, therefore, to be simple substitution products of the vinyl base.

Although perhaps improbable (compare Kipping and Salway, J., 1904, **85**, 438), it was not impossible that these two substances were stereoisomeric. The molecule of vinyldiacetonamine contains an asymmetric carbon group; unless, therefore, the three valencies of the nitrogen atom are symmetrically situated and in the same plane as the two carbon atoms with which the >NH group is directly united, there should exist stereoisomeric *dl*-vinyl bases and corresponding stereoisomeric *dl*-benzoyl derivatives. As is well known, Ladenburg claimed to have converted coniine into a stereoisomeric *iso*coniine (*Ber.*, 1893, **26**, 854), and *l*-stilbazoline into an analogous *iso*stilbazoline (*Ber.*, 1904, **37**, 3688); as vinyldiacetonamine is closely analogous to both these bases as regards the possible existence of stereoisomerides of the type under consideration, the further

| –NH·CHMe– | –NH·CHPr– | –NH·CH($CH_2$·$CH_2$Ph)– |
|---|---|---|
| Vinyldiacetonamine. | Coniine. | Stilbazoline. |

examination of the isomeric benzoyl derivatives was obviously desirable.

The first alternative to be considered was that one of the compounds might be an *O*-benzoyl derivative, produced from an enolic form of vinyldiacetonamine; qualitative experiments, however, seemed to show that both benzoyl derivatives reacted with semicarbazide in a normal manner. Such attempts to prove indirectly that both compounds were *N*-benzoyl derivatives were not

carried further, because it was found that both, when heated, gave a large proportion of benzamide and benzonitrile; it was scarcely possible, therefore, that either of these compounds could be an *O*-benzoyl derivative.

The conditions under which the two benzoyl derivatives were formed seemed to show that the compound m. p. 156° could be converted into the isomeride by heating it with benzoyl chloride; experiments confirmed this view. It was found, however, that the transformation could not be brought about by heating the compound of higher melting point with benzoyl chloride alone in benzene solution, but that it did occur if the solution also contained hydrogen chloride.

Up to this stage, the experimental evidence pointed rather to stereoisomerism; but the conversion of the one compound into the other by the action of hydrogen chloride suggested another possibility. On the assumption that the original benzoyl derivative combines with hydrogen chloride with fission of the closed chain, and that the additive product then loses a molecule of hydrogen chloride, the benzoyl derivative melting at 110° would be derived from an open-chain olefine. Experiments then showed that whereas the original benzoyl derivative is stable towards bromine and towards permanganate at the ordinary temperature, the isomeride combines immediately with the halogen and immediately reduces the permanganate. The two compounds, therefore, are no doubt structurally isomeric; the one is a simple *N*-benzoyl derivative of vinyldiacetonamine, the other in all probability an unsaturated open-chain substance, probably represented by the formula $PhCO{\cdot}NH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH{:}CHMe$ or

$$CMe_2{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}NH{\cdot}COPh.$$

As the benzoyl derivatives ceased to be of so much interest when it was found that they were not stereoisomeric, and as one of the authors could not continue their investigation, experiments to determine the structure of the open-chain isomeride have not been made. The nature of the non-nitrogenous portion of the decomposition products of the two benzoyl derivatives is also uncertain; apparently the decomposition of both substances takes place in two ways, $C_{15}H_{19}O_2N = C_6H_5{\cdot}CO{\cdot}NH_2 + C_8H_{12}O$ and

$$C_{15}H_{19}O_2N = C_6H_5{\cdot}CN + H_2O + C_8H_{12}O,$$

but whether the non-nitrogenous product is a definite compound $C_8H_{12}O$, or a mixture, is a matter for further study. The conversion of *N*-benzoyldiacetonamine into an open-chain isomeride recalls the work of Shaw (this vol., p. 1930) on the fission of the pyridine nucleus and also the conversion of quinoline into *o*-benzoylaminocinnamaldehyde by the action of benzoyl chloride and sodium

hydroxide solution (Reissert, *Ber.*, 1905, **38**, 1603, 3415). The fact that vinyldiacetonamine in alkaline solution does not give either of the benzoyl derivatives described above seems to show that some profound decomposition of the base occurs.

## Experimental.

N-*Benzoylvinyldiacetonamine*.—Freshly distilled benzoyl chloride (1 mol.) free from hydrogen chloride, is added to vinyldiacetonamine (2 mols.) which has been dried with potassium carbonate and then distilled under reduced pressure.* A development of heat occurs, the mixture becomes very viscous, and crystals soon begin to separate; when gently warmed on the water-bath for 1 hour, the whole changes into a nearly solid mass. The product is ground and extracted with cold ether; the residue consists of a mixture of the *N*-benzoyl derivative (yield 70%) and vinyldiacetonamine hydrochloride (yield nearly theoretical, both being calculated from the equation, p. 2612), which are separated by treatment with water; the ethereal extract, on evaporation, yields a yellow oil, smelling of benzonitrile. In some experiments in which the vinyl base was not very carefully dried prior to distillation, small quantities of *vinyldiacetonamine benzoate* (m. p. 92—93°) were isolated.

*N*-Benzoylvinyldiacetonamine crystallises from aqueous alcoho in long, colourless, rectangular prisms, m. p. 155—156°; it is practically insoluble in water or light petroleum, sparingly soluble in ether or carbon tetrachloride, and freely soluble in alcohol or acetone (Found: C = 73·6; H = 8·0; N = 6·1, 6·0; *M*, cryoscopic in benzene, = 243. Calc. for $C_{15}H_{19}O_2N$, C = 73·6; H = 7·8; N = 5·7%; *M* = 245).

The benzoyl derivative is readily soluble in concentrated hydrochloric acid and is not precipitated on the addition of water, but crystallises when the solution is neutralised; when it is boiled with the concentrated acid during 2 hours, the compound seems to be entirely decomposed into benzoic acid, ammonia, and a volatile oil, which from its behaviour towards phenylhydrazine appears to consist of, or to contain, a ketone. Although vinyldiacetonamine hydrochloride is not decomposed appreciably when it is boiled with hydrochloric acid, this salt is not found among the decomposition products of the benzoyl derivative; presumably, therefore, the latter is converted into the isomeride, m. p. 110°, before the benzoyl group is eliminated.

When treated with hydroxylamine hydrochloride and sodium acetate in aqueous alcoholic solution at the ordinary temperature,

* The base thus purified boils at 136—137°/120 mm., and its odour is far less pungent than that of samples less carefully dried and distilled under atmospheric pressure.

the benzoyl derivative gives a compound, doubtless the oxime, m. p. 183—184° after recrystallisation from acetone–carbon tetrachloride; with semicarbazide hydrochloride under similar conditions, the benzoyl derivative gives a sparingly soluble compound which crystallises from boiling alcohol in slender needles, m. p. 186—187°.

*N-Benzoylaminomethylheptenone*?—When vinyldiacetonamine is heated on the water-bath during several hours with benzoyl chloride (slightly more than 1 mol.) in an open flask, the product is a yellow or brown pasty mass of crystals; after warming this paste with water to remove vinyl salt and then digesting it with cold dilute alkali, there remains a thick oil which gradually, but only partially, solidifies. The crystalline portion, freed from oil on porous earthenware, separates from ether–methyl alcohol in colourless, ill-defined, lustrous crystals, m. p. 110—111°; the yield is poor, but probably a considerable proportion of the substance remains in the oily by-product.

This benzoyl derivative crystallises from aqueous alcohol in needles; it is very readily soluble in alcohol, acetone, or benzene, only sparingly soluble in cold ether or carbon tetrachloride, and practically insoluble in cold light petroleum (Found: C = 73·4; H = 7·9; N = 5·7, 5·8; *M*, cryscopic in benzene, = 243. Calc. for $C_{15}H_{19}O_2N$, C = 73·4; H = 7·8; N = 5·7%; *M* = 245).

Its behaviour with concentrated hydrochloric acid is like that of the isomeride described above. With semicarbazide hydrochloride and sodium acetate in aqueous alcoholic solution, the benzoyl derivative gives a compound which separates in prismatic crystals, m. p. about 200°.

*Decomposition of the Two Benzoyl Derivatives.*—*N*-Benzoylvinyldiacetonamine decomposes when it is heated and at about 170° (thermometer in the vapour) a liquid begins to pass over; some ammonia seems to be evolved towards the end of the decomposition and practically the whole of the benzoyl derivative is finally converted into volatile products. Those portions collected from 170° to 220° remain liquid, but the fraction, b. p. 220—250°, solidifies almost completely and consists of practically pure benzamide. From the liquid decomposition products, by fractional distillation, a portion boiling at about 190°, which appears to be pure benzonitrile, can be isolated. The fractions of lower boiling point, however, contain one or more substances which reduce alkaline permanganate at the ordinary temperature, giving potassium salts of volatile fatty acids. It is very probable, therefore, that this oil contains some open-chain unsaturated ketone closely related to a methylheptenone.

So far as could be ascertained when the benzoyl derivative,

m.p. 110—111°, is heated, it gives the same decomposition products as *N*-benzoylvinyldiacetonamine; benzamide was definitely identified and the liquid fractions contained benzonitrile.

*Conversion of N-Benzoylvinyldiacetonamine into the Isomeride.*—*N*-Benzoylvinyldiacetonamine (5 g.), heated in an open flask on the water-bath with an equal weight of benzoyl chloride during about 3 hours, gives a yellowish-brown oil; when freed from benzoyl chloride and benzoic acid, and then from volatile products (benzonitrile, etc.) by steam distillation, the residue (5 g.) separates from ether in colourless crystals (yield about 2·5 g.), m. p. 110—111°, which are identical with those of the benzoyl derivative already described.

*N*-Benzoylvinyldiacetonamine (2 g.), heated in benzene solution (12 c.c.) in absence of moisture with 20—30% of its weight of benzoyl chloride free from hydrogen chloride, seems to undergo no change in the course of 3 hours; when, however, the solution is saturated with hydrogen chloride and heated again during 3 hours, the product, freed from benzoyl chloride and a small proportion of oily matter, separates from aqueous alcohol in crystals, m. p. 110—111°.

*The two benzoyl derivatives are structurally isomeric.* *N*-Benzoylvinyldiacetonamine, in cold carbon tetrachloride solution, does not react with bromine to an appreciable extent, whereas the isomeride combines readily with the halogen In the latter case, the carbon tetrachloride solution, when evaporated at the ordinary temperature, gives a viscous oil. The difference in behaviour between the two benzoyl derivatives towards potassium permanganate solution is even more striking; finely divided *N*-benzoylvinyldiacetonamine, suspended in a dilute cold solution of the reagent, brings about no visible change even after the expiration of 3 days; under similar conditions,the isomeride causes an immediate and pronounced reduction of the reagent.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 28th,* 1924.]

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## CCCLVII.—*Organic Derivatives of Silicon. Part XXXI. Action of Mercuric Oxide on Diaryldichlorosilicanes.*

By LEONARD REGINALD VYLE and FREDERIC STANLEY KIPPING.

SOME of the more noticeable differences between corresponding derivatives of carbon and silicon have been observed during investigations of the disubstituted silicols, $SiR_2(OH)_2$, produced by

the hydrolysis of the dichlorides, $SiR_2Cl_2$; although not very stable, these diols can be obtained in a pure crystalline state, provided possibly that one of the hydrocarbon radicals is aromatic (Robison and Kipping, J., 1912, **101**, 2156). The difference in stability between these compounds and the corresponding derivatives of carbon is, perhaps, less noteworthy than the difference in the manner in which they undergo decomposition; so far as is known, the dehydration of a silicanediol never gives a simple silicone, $R_2SiO$, corresponding with a ketone, but results in the formation of one or more condensation products,

$$HO{\cdot}SiR_2{\cdot}O{\cdot}SiR_2{\cdot}OH,\ HO{\cdot}SiR_2{\cdot}O{\cdot}SiR_2{\cdot}O{\cdot}SiR_2{\cdot}OH,$$

etc.; which may pass into closed-chain compounds by a further loss of the elements of water; diphenylsilicanediol, for example, gives four well-defined crystalline condensation products (Kipping, J., 1912, **101**, 2125), but in this, as in other cases, there is no evidence of the production of the simple silicone.

Since the direct elimination of a molecule of water from 1 mol. of a disubstituted silicanediol seems to be impossible, just as is, apparently, such a change in the case of compounds $SiR(OH)_3$ (Meads and Kipping, J., 1914, **105**, 679; 1915, **107**, 459) and in that of orthosilicic acid itself, the preparation of the simple silicones was attempted by the action of certain metallic oxides on the dichlorides $SiR_2Cl_2$. Diphenyldichlorosilicane, in toluene solution, reacts readily with mercuric oxide, giving mercuric chloride; the product contains some trianhydrotrisdiphenylsilicanediol (Kipping, *loc. cit.*), mercuric phenyl chloride, and silica, but consists essentially of a viscous oil. The formation of trianhydrotrisdiphenylsilicanediol is analogous to the production of trioxymethylene from methylene di-iodide and silver oxide; it seems probable that, in the case of the silicon compound, at any rate, this reaction takes place in a series of stages, in which the intermediate products are $SiPh_2Cl{\cdot}O{\cdot}SiPh_2Cl$ and $SiPh_2Cl{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2Cl$, corresponding with anhydrobis- and dianhydrotris-diphenylsilicanediol respectively. The production of mercuric phenyl chloride and silica seems to be due to the decomposition of trianhydrotrisdiphenylsilicanediol, or other similar compounds, by mercuric oxide, with the formation of mercury diphenyl and silica, and the subsequent interaction of mercury diphenyl and mercuric chloride to give mercuric phenyl chloride, a change which is known to occur in alcoholic solution.

The main product, the viscous oil, when freed as far as possible from trianhydrotrisdiphenylsilicanediol and from diphenyl (impurity in the dichloride) contains 14·3—14·4 % of silicon; since $SiPh_2O$ requires 14·4 %, it seemed that this oil might be the simple silicone. Such a substance, however, would no doubt be volatile in steam and

this product was not. That it consisted entirely of one or more compounds $(SiPh_2O)_n$ was proved by its behaviour towards alcoholic potassium hydroxide solution, by which it was converted, except for a negligible residue, into diphenylsilicanediol. These results could be explained by assuming that the simple silicone is actually formed by the action of mercuric oxide on the dichloride but that it combines with water to form the diol, which then undergoes condensation in the usual manner, giving the four known, and possibly other, condensation products; against such an assumption there was the fact that only one of these condensation products had actually been separated from the oil, and this only in small quantities. To test this question, the original toluene solution of the whole of the products was directly submitted to distillation (30 mm.); at about 310° some trianhydrotrisdiphenylsilicanediol collected in the receiver, but no visible ebullition occurred and no other silicon compound volatilised. It must be concluded therefore that the simple silicone was not present in the original product, or else had undergone polymerisation when it was heated.

The transformation of a simple silicone into complex compounds $(SiPh_2O)_n$ without the intermediate formation of the dihydroxy-derivative may no doubt be regarded as a possibility, inasmuch as the polymerisation of aldehydes does not apparently require the intermediate production of a glycol; but even admitting that such a change is possible, the nature of the glue-like substance, $(SiPh_2O)_n$ or mixture, obtained from the dichloride is obscure. Its non-volatility proves that the value of $n$ must be greater than 3, and it can hardly be 4 because tetra-anhydrotetrakisdiphenylsilicanediol $(SiPh_2O)_4$, if present even in relatively small proportions, could scarcely have escaped detection. Cryoscopic results point to the molecular formula $(SiPh_2O)_8$.

The action of mercuric oxide on dibenzyldichlorosilicane was also studied. The reaction in hot toluene did not proceed so rapidly as in the case of the diphenyl derivative, but the main product was a thick oil from which trianhydrotrisdibenzylsilicanediol (Robison and Kipping, *loc. cit.*) could be isolated; no mercuric benzyl chloride was produced, owing apparently to the fact that trianhydrotris-dibenzylsilicanediol and other silicones $[Si(CH_2Ph)_2O]_n$, unlike the diphenyl compounds, are not acted on by mercuric oxide to give mercury dibenzyl. The principal product contained Si = 12·3 [$Si(CH_2Ph)_2O$ requires Si = 12·5 %] and when boiled with an alcoholic solution of potassium hydroxide it was completely converted into dibenzylsilicanediol: when the toluene solution of the crude product was directly submitted to distillation (30 mm.), a little trianhydrotrisdibenzylsilicanediol collected in the receiver,

but no other silicon compound volatilised. The glue-like product from dibenyzlsilicon dichloride is consequently analogous to that from the diphenyl derivative; it may perhaps contain some tetra-anhydrotetrakisdibenzylsilicanediol, which is not known, but as this compound would probably be sparingly soluble and crystallise readily, its presence in the readily soluble oil seems to be improbable.

It must be concluded, therefore, that the products from both the dichlorides consist of highly complex molecules $(SiR_2O)_n$ containing closed chains of more than four atoms of silicon and four atoms of oxygen; the facts that they do not crystallise and are readily soluble in many common organic solvents are difficult to reconcile with this view, even on the assumption that both products are mixtures; their non-volatility and the results of the crysocopic determinations, however, leave no alternative. The possible existence of molecules $(SiR_2O)_n$ with a value of $n$ greater than 5 is confirmed by results obtained previously with diethylsilicone (Martin and Kipping, J., 1909, **95**, 313), the molecular weight of which was found to be 694 in benzene solution (cryoscopic), the calculated value for $SiEt_2O$ being 102; this silicone, moreover, is miscible with many organic liquids.

## Experimental.

*Diphenyldichlorosilicane and Mercuric Oxide.*—When a toluene solution of diphenyldichlorosilicane is boiled under reflux with scarlet mercuric oxide (1·05 mols.) for about 30—40 minutes, a small separation of crystals sometimes occurs, the mercuric oxide becomes brown, and only a very small proportion of the unchanged dichloro-compound is present, since very little diphenylsilicanediol is extracted by a solution of sodium hydroxide; to complete the decomposition of all chlorosilicon derivatives, however, the boiling must be continued during a further period of about an hour. The suspended matter, consisting of mercuric chloride, unchanged oxide, a little mercuric phenyl chloride, and very small proportions of silica and calomel, is separated and washed with toluene; the filtrate and washings on evaporation give a thick, yellow "glue," from which, by fractional crystallisation from alcohol–acetone, trianhydrotrisdiphenylsilicanediol (m. p. 188°) and mercuric phenyl chloride (m. p. 250°) can be isolated in small quantities; the crystalline silicon compound forms perhaps about 2 % of the total products. When, in order to remove completely the rest of the mercuric phenyl chloride and also the diphenyl (impurity in the silicon dichloride), the oily product is distilled in steam, no silicon compound volatilises; the aqueous solution, which contains some mercuric chloride, is decanted from the non-volatile, glue-like residue, and the latter is

dissolved in acetone. The product from the acetone solution, dried at 100°, is free from mercury compounds and has the composition $SiPh_2O$. Found Si = 14·38 as the average of four concordant analyses with different samples. Required Si = 14·4 %. $M$ = 1605 (cryoscopic in benzene).

This product is very readily soluble in the common organic solvents with the exception of the lower alcohols and light petroleum, in which it is only sparingly soluble; when fractionally precipitated from acetone, benzene, ether, etc., with alcohol or light petroleum, it gives no crystalline compound other than those mentioned above. It does not give hydrogen when it is warmed with an aqueous acetone solution of potassium hydroxide or with piperidine and water, but it is hydrolysed by the former and after three operations about 98 % of it is converted into the soluble potassium derivative of diphenylsilicanediol.

The thick, yellow "glue" from the toluene solution (see above), submitted directly to distillation (30 mm.), gives only about 2—3 % of its weight of volatile products even when it is heated at 350°; the distillate contains diphenyl, mercuric phenyl chloride, mercuric chloride, and trianhydrotrisdiphenylsilicanediol, but no true ebullition is observed during the operation. The residue, which probably still contained some trianhydrotrisdiphenylisilicanediol, gave $M$ = 1345 (cryoscopic in benzene) as the average of 3 concordant results.

Most of the mercuric phenyl chloride which is formed in the above described reaction remains in the residue of mercuric chloride and oxide, although some of it is contained in the toluene filtrate. The residue is extracted with boiling alcohol and the extract poured into a large volume of water. The precipitated mercuric phenyl chloride, recrystallised from acetone–alcohol, is obtained in colourless plates, m. p. 250°; treated with potassium iodide in boiling aqueous solution, it gives a colourless, crystalline compound, m. p. 264°, which is the melting point of mercuric phenyl iodide.

*Trianhydrotrisdiphenylsilicanediol and Mercuric Oxide.*—The mercuric phenyl chloride obtained in the reaction with the diphenyldichlorosilicane does not seem to be formed directly in accordance with the equation $SiPh_2Cl_2+2HgO=2HgPhCl+SiO_2$, but is probably produced from the trianhydrotrisdiphenylsilicanediol or some other silicone in the following manner: $(SiPh_2O)_n + nHgO = nHgPh_2+nSiO_2$ and $HgPh_2+HgCl_2=2HgPhCl$.

This inference is based on the fact that trianhydrotrisdiphenylsilicanediol in boiling toluene solution is attacked by mercuric oxide, giving silica and mercury diphenyl; under these conditions the reaction takes place very slowly, but when trianhydrotrisdiphenyl-

silicanediol is heated with excess of mercuric oxide at about 200°, mercury diphenyl sublimes and the reaction is complete after about 90 minutes; it is known that mercury diphenyl reacts with mercuric chloride in alcoholic solution, giving mercuric phenyl chloride and it was proved that the same change occurs in toluene solution. The glue-like product obtained from the diphenyldichlorosilicane, freed from mercuric phenyl chloride by steam distillation and from trianhydrotrisdiphenylsilicane so far as possible by fractional precipitation, also gives mercury diphenyl when it is heated with mercuric oxide in toluene solution; after evaporating the solvent and submitting the residue to distillation in steam, mercury diphenyl passes over, but whether this volatile compound has been formed from trianhydrotrisdiphenylsilicanediol or from more complex silicones cannot be ascertained with certainty, as the whole of the former may not have been removed from the glue-like product.

*Dibenzyldichlorosilicane and Mercuric Oxide.*—A reaction takes place between mercuric oxide and dibenzyldichlorosilicane under the same conditions as those used in the case of the diphenyl compound, but the toluene solution must be heated during about 6 hours before the whole of the dichloride is decomposed. The unchanged mercuric oxide, traces of calomel and silica, and most of the mercuric chloride are separated by filtration, and the toluene solution is evaporated; the residue is a thick, glue-like substance. This product, submitted directly to distillation (30 mm.), gives a very small proportion of dibenzyl and stilbene (impurities in the dichloride), and mercuric chloride then sublimes; later, a little trianhydrotrisdibenzylsilicanediol passes over, but there is no appearance of ebullition and the total volatile matter forms only about 1 % of the whole. The presence of mercuric benzyl chloride in the distillate could not be detected; its non-formation is doubtless due to the fact (see below) that trianhydrotrisdibenzylsilicanediol and also the more complex glue-like dibenzylsilicones do not react with mercuric oxide to form mercury dibenzyl even at 200°; incidentally this fact, and the non formation of mercuric benzyl chloride, support the explanation suggested above as to the manner in which the mercuric phenyl chloride is produced from the diphenyldichlorosilicane.

In order to determine the composition of the main product, the glue from the toluene solution is freed from dibenzyl and stilbene by steam distillation and is then fractionally precipitated from its acetone solution with alcohol. Repeated operations give a small proportion of trianhydrotrisdibenzylsilicanediol (m. p. 98°), but no matter what solvent or mixture of solvents is used practically the whole of the material invariably separates as a thick oil which

dissolves very readily in ether, acetone, benzene, etc., but is only sparingly soluble in alcohol or light petroleum. This oil, freed from solvent at 100°, has the composition $Si(CH_2Ph)_2O$ (Found: Si = 12·35, 12·30; required Si = 12·5 %); like the product from diphenyldichlorosilicane, it must be regarded as a highly complex dibenzylsilicone, or as a mixture of such compounds.

Trianhydrotrisdibenzylsilicanediol does not react with mercuric oxide in boiling toluene solution, and even when it is heated with mercuric oxide alone at 200° no volatile mercury compound is formed; the glue-like dibenzylsilicone shows a similar behaviour.

The oxides of cadmium and of silver do not seem to react with diphenyldichlorosilicane.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant which enabled them to obtain supplies of diphenyl- and dibenzyl-dichlorosilicane from Boots Pure Drug Co.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, October 17th,* 1924.]

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## CCCLVIII.—*An X-Ray Investigation of the Lower Members of the Fatty Acid Series.*

By REGINALD EDMUND GIBBS.

RECENT *X*-ray analysis of some fatty acids (Müller, J., 1923, **123**, 2043; Piper, *Proc. Phys. Soc.*, 1923, **200**) showed that one of the observed spacings increased proportionately with the number of carbon atoms, from 10 to 22 in the formula.

These measurements have now been extended to the lowest members of the series in order to find at what point the proportionality law failed. As in Müller's experiments, powder reflection photographs were taken using a gas tube with a copper anticathode run at about 40 K.V. and 5 m.a. The distance between the axis of rotation and the plate was 7·55 cm., the slit was 0·2 mm. wide, and an exposure of about 2 hours was made on each side of the centre.

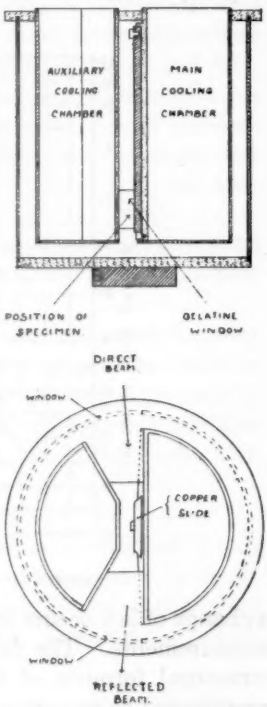
It was found that the long spacings were detected most easily with well-formed, thin layers, whilst the side spacings were seen best when the molecular chain became more nearly parallel to the surface on which the specimen was set. For solids such as stearic acid, this was shown by cutting a thin slip ¼ mm. thick from a 3 mm. layer and laying it on its side.

Some difficulty was experienced in obtaining suitable layers for the acids which were liquid at the ordinary temperature. Two methods were employed, either the liquid layer was frozen *in situ*,

in which case it was necessary to keep it spread out during the actual freezing, or the liquid was first frozen and then a layer made as for any powder. The second method gave better records of the smaller spacings. The chief difficulty was to avoid the deposit of ice on the apparatus and specimen. The specimen was prepared as rapidly as possible on a copper slide, which was inserted from the top into the apparatus shown.

The slide fitted against the side of the main cooling chamber and opposite to an auxiliary chamber maintained at a slightly lower temperature. A test of this procedure when moisture was purposely admitted showed the one surface covered with ice to a depth of several millimetres while the other was quite clear. This method was useful only for substances having low vapour pressures. Two windows covered with thin gelatin will be seen in the outer brass case on a level with the specimen. They were about 1 cm. high and wide enough to enable any spacings above about 2 Å.U. to be measured.

FIG. 1.




Measurements were made on the first ten acids, and check plates taken of ice and mica; the acids were placed sometimes on the latter for calibration purposes. The ice lines, being in the neighbourhood of the side spacings, were carefully considered. However, the undoubted existence of the 3·68 line for the acids which are normally solid, suggests that here also this line arises from the acid and not from the ice. The results can be stated briefly as follows :—

| Name. | N. | M.P. | $d_1$. | $d_2$. | | $d_3$. | $d_4$. |
|---|---|---|---|---|---|---|---|
| Decoic ..... | 10 | 30° | 23·3 Å.U. | 4·14 | | 3·73 | |
| Octoic ..... | 8 | 16·5 | 19·0 | 4·14 | | 3·65 | 3·48 |
| Hexoic ..... | 6 | — 2 | 14·6 | 4·14 | | 3·65 | 3·47 |
| Butyric ..... | 4 | — 4 | 9·65 | 4·09 | | 3·65 | 3·45 |
| Acetic ..... | 2 | 16·5 | 6·66 | | | | |
| Nonoic ..... | 9 | 10 | 22·9 | 4·22 | 3·97 | 3·71 | 3·48 |
| Heptoic ..... | 7 | —10 | 16·4 | 4·29 | 3·97 | 3·75 | 3·49 |
| Valeric ..... | 5 | —58·5 | 10·1 ? | | | | |
| Propionic ..... | 3 | —36·5 | 6·75 | 4·03($\frac{1}{2}$) | | | 3·43($\frac{1}{2}$) |
| Formic ..... | 1 | 7·5 | 5·19 | | | | |

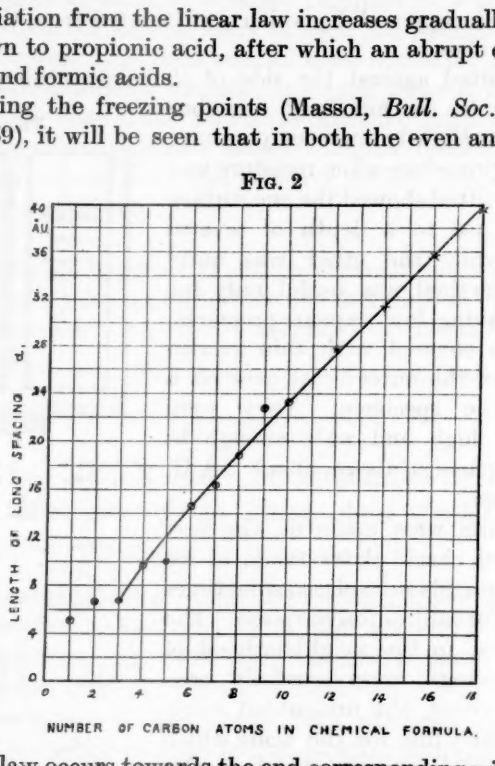
The sign ($\frac{1}{2}$) indicates that the line was obtained only on one side of the centre.

Several attempts were made to obtain a photograph of valeric acid, but with little success. This acid is especially subject to extensive supercooling, and as the apparatus was not designed to attain a very low temperature it is quite possible that the liquid was not frozen.

The deviation from the linear law increases gradually from about hexoic down to propionic acid, after which an abrupt change occurs for acetic and formic acids.

Considering the freezing points (Massol, *Bull. Soc. chim.*, 1895, [iii], **13**, 759), it will be seen that in both the even and odd groups

FIG. 2




a change of law occurs towards the end corresponding with the *X*-ray measurements. The failure of the linear law was expected; the structural formula of formic acid, for example, enables it to be represented as an acid or an aldehyde and it was almost certain that the structure at this stage would be seriously affected by the addition of each $CH_2$ group.

The interpretation of the failure of the law depends on the constancy or otherwise of the true side spacings, *e.g.*, if the molecular widths remain constant but the length varies non-linearly, then it may mean either that the uniform chain has not yet been reached or that the length increments are constant but the angle of tilt of the molecule is altering.

As in Müller's work, the side spacings are always represented by wider and more diffuse lines than are the main spacings. With the

lowest members, it became increasingly difficult to define which were the corresponding length and side spacings, whilst if the structure changed fundamentally no correspondence could be expected. The side spacings for the even acids change only to a small extent. The results for the odd acids are more difficult to correlate and are given only as isolated readings; they seem to display less regularity than the even ones, indicating a departure probably from the regular structure of the latter. For both types, and particularly the odd acids, some more spacings are recorded.

Referring to Müller and Shearer (J., 1923, **123**, 3156), three possible types of chain, all conserving the diamond tetrahedral angle, are discussed, and it is shown that the even acids may follow the third type in which the increase per two carbon atoms is 2 Å.U. as required by the linear relation. It may be pointed out that for the odd acids also there is an attempt at regularity, for an increase of carbon atoms from $N$ to $N + 4$, where $N$ is odd, increases the length of the double chain by about 9·6 Å.U., *i.e.*, 2·4 Å.U. per two carbon atoms.

The full increase, 9·6, for the two carbon atoms appears to take place in two parts, *viz.*, of approximately 6·4 or 3·2 Å.U. for a pair of carbon atoms.

Owing to the doubt that has existed as to the nature of the fatty acids, it is of interest to note that since this paper was written further work has been done with stearic acid showing it to be of a true crystalline nature and demonstrating its extinction directions and brush figures. Several single crystal $X$-ray photographs of it have already been taken.

In conclusion, I wish to express my thanks to Sir William Bragg for his helpful criticism and the interest he always extends to my work. I desire also to acknowledge my appreciation of the grant from the Scientific and Industrial Research Department which enabled this work to be undertaken.

DAVY FARADAY RESEARCH LABORATORY. [*Received, October 25th*, 1924.]

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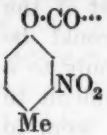
## CCCLIX.—*Substituted Carbonates derived from* p-*Cresol.*

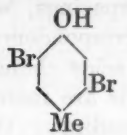
By ROLAND HALL GRIFFITH.

THE nitration of ditolyl carbonate, which has been investigated by Holleman (*Rec. trav. chim.*, 1917, **36**, 271), gives rise mainly to the **3** : **3**′-dinitro-carbonate (I). The present communication

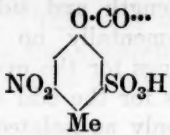
is concerned with the further substitution of this substance and also



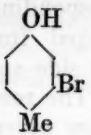
(I.)



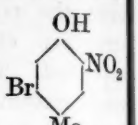
(II.)



(III.)



(IV.)



(V.)

with the behaviour of the corresponding dibromo-carbonate. Hiratsuka found (unpublished work) that it is not possible to obtain the symmetrical tetranitro-carbonate by further nitration of the dinitro-compound, and attempts to prepare 5 : 5′-dibromo-3 : 3′-dinitroditolyl carbonate by halogenation of the dinitro-carbonate have now resulted in the formation of a tetrabromo-carbonate. It is considered that this substance is a derivative of the dibromo-*p*-cresol (II) in view of the results obtained on nitration of the 3 : 3′-dibromo-carbonate, described below, and since the same substance was formed even without excess of bromine, the reaction appears to proceed by replacement of the nitro-groups followed by halogenation of the product.

Although nitration and bromination do not take place normally, sulphonation of dinitroditolyl carbonate occurs readily with 18% oleum. In accordance with the behaviour of the simple carbonate on nitration it may be presumed that the main product of this sulphonation is the sulphonic acid (III); the sulphonic acid of the free cresol has now been isolated as its mono- and di-potassium salts.

The action of bromine on ditolyl carbonate gives rise to a mixture of the two isomeric dibromo-carbonates, but the separation of the isomerides is difficult, and the 3 : 3′-dibromo-carbonate is best obtained by the action of carbonyl chloride on the sodium salt of the bromo-cresol (IV). This bromo-carbonate can be nitrated satisfactorily in sulphuric acid suspension, and hydrolysis of the reaction mixture gives two bromonitrocresols, one of which is volatile in steam. To this is assigned, in consequence, the structure (V) and the involatile portion must be 3-bromo-5-nitro-*p*-cresol. The powerful directing influence of the bromine atom in comparison with that of the methyl group is well demonstrated by this result.

## Experimental.

*Bromination of Dinitroditolyl Carbonate.*—A solution of the carbonate (5 g.) in 130 c.c. of sulphuric acid, after being treated with 6 g. of bromine at 100° in presence of a little iron dust, is heated for 6—8 hours. The crude reaction product obtained by pouring the mixture on to ice is hydrolysed by warming for a short time with alkali; on

acidifying the resulting solution, an oil separates which is extracted with ether and crystallised from petrol–ether. It forms pale yellow needles, m. p. 135° (Found: Br = 60·17. Calc. for $C_7H_6OBr_2$, Br = 60·15%).

*Sulphonation of Dinitroditolyl Carbonate.*—The dinitro-carbonate (5 g.) is heated with 10 c.c. of 18% oleum at 125—130° for 15 or 30 minutes. The mixture is then poured into water without any cooling precautions, so that the free cresol is liberated from its carbonate. By means of milk of lime and potassium carbonate the nitrocresolsulphonic acid in the clear solution is converted through the calcium salt into the potassium salt, which separates in pale brown crystals on evaporating the solution. This salt crystallises better from dilute alcohol in straw-coloured needles (Found: K = 13·7. Calc. for $C_7H_6O_6NSK,H_2O$, K = 13·5%). The dipotassium salt is obtained by adding potash to the alcoholic solution of the monopotassium salt; it separates from boiling alcohol in scarlet crystals and when boiled with ethyl iodide in alcoholic solution is converted into a new salt, with separation of potassium iodide; the isolation of a pure sample of this substance, presumably the ethyl ether of the nitrocresolsulphonic acid, has not been accomplished owing to the very similar solubilities of the substance and of potassium iodide.

3 : 3′-*Dibromoditolyl Carbonate.*—The sodium salt of the bromocresol is only slightly soluble in water, but dissolves in 40% aqueous alcohol; when carbonyl chloride is passed through this solution, the temperature rises and a white solid is formed. The reaction proceeds best at 40°. The washed and dried solid product, crystallised from alcohol, forms needles, m. p. 134° (Found: Br = 39·6. Calc. for $C_{15}H_{12}O_3Br_2$, Br = 40%). The isomeric 2 : 2′-dibromocarbonate can be isolated from the reaction product when ditolyl carbonate is treated with bromine in boiling carbon tetrachloride solution; it separates from alcohol in crystals, m. p. 119° (Found: Br = 39·65; calc., 40%). A mixture of the two carbonates melted at 104—105°.

*Nitration of the Dibromo-carbonate.*—Although the dibromocarbonate is not appreciably soluble in sulphuric acid, it can be nitrated in suspension; 20 g. are ground to a fine paste with sulphuric acid and the volume is gradually made up to 125 c.c. Nitration is carried out with a mixture of 10 g. of 70% nitric acid and 25 g. of sulphuric acid at 20°; as the reaction proceeds, solid passes into solution, but later separates again. The mixture is allowed to stand one hour and then poured on to ice. The solid which is produced can be crystallised from high-boiling petrol and melts at 176° (Found: Br = 32·2. Calc. for $C_{15}H_{10}O_7N_2Br_2$, Br = 32·6%).

The crude product is hydrolysed by warming with slight excess of

alkali; on adding acid and extracting with ether, an oil is obtained which can be distilled under reduced pressure, boiling at 140—160°/15 mm. About 96% of this is volatile in steam, and on crystallisation from petrol–ether forms yellow crystals, m. p. 62° (Found: Br = 34·68. Calc. for $C_7H_6O_3NBr$, Br = 34·48%). The sodium salt of this bromonitrocresol crystallises in red plates with a golden lustre from aqueous alcohol.

The portion of the reaction product involatile in steam forms a brown gum; every effort to crystallise this failed and only a small amount was obtained, but there can be little doubt that it is the isomeric bromonitrocresol.

My thanks are due to the Department of Scientific and Industrial Research, and to the Chemical Society for grants which have made possible the work in the course of which the above results were obtained.

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OXFORD. [*Received, October 17th,* 1924.]

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## CCCLX.—*Influence of Pressure on the Freezing Point of* p-*Nitrotoluene,* m-*Dinitrobenzene and Guaiacol.*

By NICOLAI ANTONOVICH PUSHIN.

DETERMINATIONS of temperature and pressure corresponding to the transition from the solid to the liquid state have been carried on by a manometric method, which consists in keeping the temperature constant and determining, by means of a manometer, the pressure at which the liquid is in equilibrium with the crystal phase (compare Tammann, "Kristallisieren und Schmelzen," 1903, pp. 192—194; Bridgman, *Physical Rev.*, 1914, **3**, 126; *Proc. Amer. Acad.*, 1912, **47**, 441; 1913, **49**, 1). In the following experiments, the substance was placed in a glass tube, sealed at one end; the other end was in a vessel with mercury (Fig. 1). The bomb was also partly filled with mercury in order to prevent contact between the substance and the castor-oil used for transfer of pressure. The temperature of the thermostat was kept constant within $\pm$ 0·02°. The results are summarised below and plotted in Fig. 2.

p-*Nitrotoluene.*—The sample used (35·65 g.) crystallised at 51·5° under atmospheric pressure.

| $t$ ..... | 51·5° | 68·0° | 75·0° | 88·0° | 100·0° | 112·0° | 125·0° |
|---|---|---|---|---|---|---|---|
| $p$(kg./cm.$^2$) | 1 | 648 | 900 | 1401 | 2080 | 2647 | 3110 |

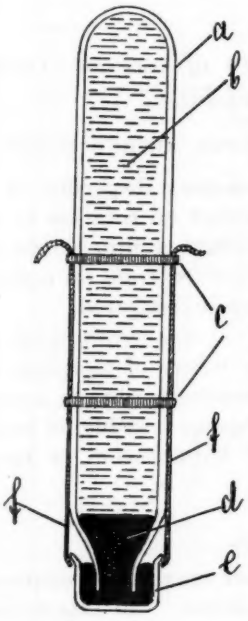
m-*Dinitrobenzene*.—The purified sample (48·61 g.) crystallised at 89·8°.

| | | | | |
|---|---|---|---|---|
| *t* ..... | 89·8° | 110·0° | 125·0° | 140·0° |
| *p*(kg./cm.²) ..... | 1 | 802 | 1414 | 2099 |

*Guaiacol*.—The purified sample crystallised at 28·3°.

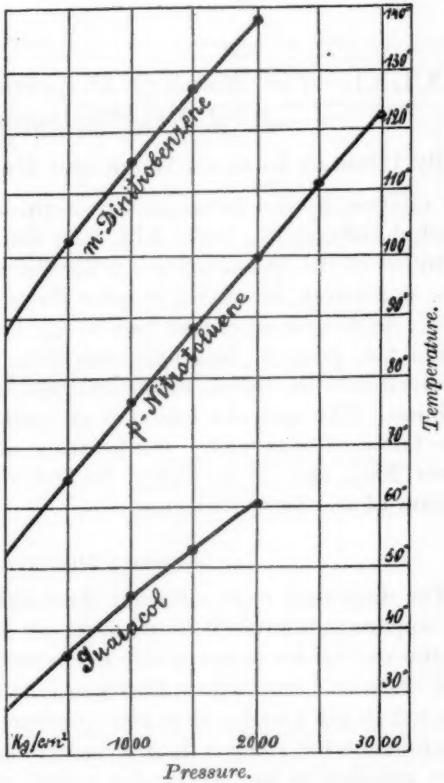
| | | | |
|---|---|---|---|
| *t* ..... | 28·3° | 45·2° | 60·1° |
| *p*(kg./cm.²) ..... | 1 | 1077 | 1981 |

FIG. 1.




*a*, glass tube.
*b*, substance.
*c*, rubber ring.
*d*, quicksilver.
*e*, glass cup.
*f*, thread.

FIG. 2.




*Pressure.*

*Influence of pressure on the temperature of crystallisation.*

Denecke (*Z. anorg. Chem.*, 1919, **108**, 1) represented the temperature of crystallisation of guaiacol at different pressures by the equation $t = 28{\cdot}4° + 0{\cdot}0178\,p - 0{\cdot}00000100p^2$. For pressures of 1000 and 2000 kg./cm.², this equation gives the values 45·2° and 60°, respectively, which are in close agreement with the values found experimentally during the present work.

Interpolation gives the following results :

| | *p*-Nitrotoluene. | | *m*-Dinitrobenzene. | | Guaiacol. | |
|---|---|---|---|---|---|---|
| *p*(kg./cm.²). | *t.* | *dt/dp.* | *t.* | *dt/dp.* | *t.* | *dt/dp.* |
| 1 | 51·5° | | 89·8° | | 28·3° | |
| 500 | 64·0 | 0·0250° | 102·4 | 0·0250° | 36·4 | 0·0161° |
| 1000 | 76·5 | | 114·8 | 0·0242 | 44·4 | 0·0161 |
| 1500 | 88·0 | 0·0231 | 126·9 | 0·0232 | 52·5 | 0·0161 |
| 2000 | 99·6 | | 138·0 | | 60·5 | |
| 2500 | 111·1 | 0·0228 | | | | |
| 3000 | 122·4 | | | | | |

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## CCCLXI.—*The Rotatory Dispersion of certain Normal Alkyl Hexahydromandelates.*

By CHARLES EDMUND WOOD and MERVYN ARTHUR COMLEY.

IN relation to the investigation of the rotatory dispersion of the *n*-alkyl lactates (J., 1923, **123**, 600) the effect on rotation of substitution of the *cyclo*hexyl group for the methyl group of lactic acid was of interest, for no alkyl ester series derived from an optically active hydroaromatic acid had so far been investigated.

For this purpose, hexahydromandelic acid was synthesised, and resolved into its optical enantiomorphs by means of morphine and quinine. The optical rotation of the nine esters (methyl to *n*-nonyl) was taken over as wide a temperature range as possible, in certain cases 200°, this range being limited by vaporisation or racemisation of the particular ester.

### *Rotatory Dispersion.*

The dispersion curves do not show either maxima or minima or an apparent approach to maxima or minima. No intersections of the curves for a particular ester occur; further, a continuous and distinct spreading of the curves takes place on passing from the red to the violet end of the spectrum, that is to say, the larger the rotation the steeper the tangential angle made with the axis of zero rotation at any particular wave-length.

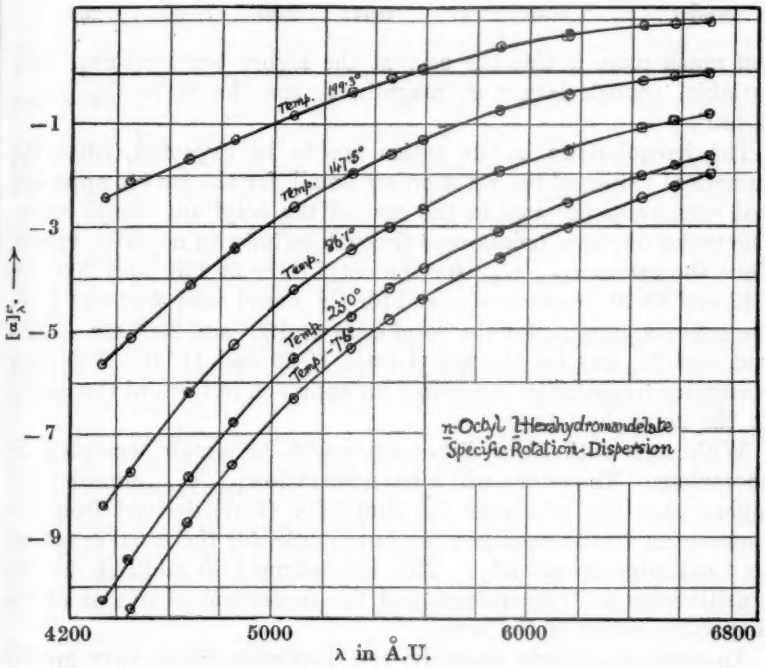
The curves for the octyl lævo-ester are shown in Fig. 1, an interesting feature being that the curves for the highest temperature recorded cross the zero axis towards the red end of the spectrum.

On comparing our results with the analysis of the Drude equation by Hunter (this vol., p. 1198), cases III and IV, which involve two terms of opposite sign, are applicable. At low temperatures $k_0 > k_1$ when $\lambda_0 > \lambda_1$; the curves then lie completely in the region of negative rotation. With increasing temperature, $k_0$ and $k_1$ vary, $k_0$ becoming equal to, and finally less than $k_1$; the curves

then cross the axis into the region of positive rotation. The same conditions with reversal of sign hold for the nonyl dextro-ester. In these esters the crossing of the axis has been realised in the visible region, but we could not detect a maximum such as is to be expected in the red end of the spectrum, owing probably to the limits of visual observation.

The rotatory dispersion exhibited by all the esters is of a similar type, normal and complex. The nearest approach to simplicity, if simplicity is realisable (Hunter, *loc. cit.*), is shown by the methyl

FIG. 1.




ester at − 12°. As the series is ascended, in general, the numerical value of the rotation diminishes, and the dispersion approaches the condition for anomaly.

The dispersion of the *l*-hexahydromandelates is closely allied to that of the lactates, but a point of difference is that the curves for the former are convex on the negative side, and for the latter convex on the positive side, to the axis of zero rotation.

In the first column of Table I, the ratio on ascending the series tends sensibly to a constant value, but this is not maintained in the other ratios given. Even at 30°, where the rotation values are more remote from the axis, the ratio $\alpha_{6708}/\alpha_{5461}$ is very variable,

TABLE I.

*Dispersion Ratios.*

| | At 30°. | | | At 140°. | | |
|---|---|---|---|---|---|---|
| Ester. | λ 4359. | 5461. | 6708. | 4359. | 5461. | 6708. |
| Methyl ..... | 1·72 | 1 | 0·500 | 1·80 | 1 | 0·601 |
| Ethyl ..... | 2·00 | 1 | 0·576 | 1·98 | 1 | 0·555 |
| Propyl ..... | 2·04 | 1 | 0·518 | 2·44 | 1 | 0·418 |
| Butyl ..... | 2·03 | 1 | 0·523 | 2·24 | 1 | 0·422 |
| Amyl ..... | 2·31 | 1 | 0·465 | 2·58 | 1 | 0·416 |
| Hexyl ..... | 2·17 | 1 | 0·392 | 3·09 | 1 | 0·192 |
| Heptyl ..... | 2·34 | 1 | 0·501 | 2·69 | 1 | 0·232 |
| Octyl ..... | 2·47 | 1 | 0·372 | 3·46 | 1 | 0·080 |
| Nonyl ..... | 2·36 | 1 | 0·442 | 2·50 | 1 | 0·265 |

and much more is this the case at the higher temperature. Less variable, though larger in magnitude, are the ratios $\alpha_{4359}/\alpha_{5461}$ at 140°.

The irregularities in the ratios are to be expected, since the numerical values of the rotation are small, for the curves approach and even cross the axis in the case of the octyl and nonyl esters. The ratios at these points pass through infinity to negative values. Thus the ratios $\alpha_{4359}/\alpha_{5461}$ for the octyl ester at 190° and 200° are 7·42 and 19·20, respectively, and for the nonyl ester 4·03 and 5·74; the ratios $\alpha_{4359}/\alpha_{5893}$ for the octyl ester at 190° and 200° are − 10·5 and − 4·22, and for the nonyl ester 16·80 and 117·0. A further reason for irregularity is possibly an approach in form of the curves to the anomalous type.

With such ratios the dispersion might be simple, complex, or anomalous. The esters, which have the ratio $\alpha_{4359}/\alpha_{5461}$ considerably higher than the minimum for simplicity (1·57) derived from the single-term Drude equation, are not simple, for the usual graphical test indicates complexity. This is confirmed in addition by the sensitiveness to temperature, and the inconstant character of the dispersion ratios of the series.

In cases of obvious anomaly, the dispersion ratios vary greatly when the dispersion curve crosses the axis of zero rotation, which, up to the present for compounds in the homogeneous condition, has been observed in the violet region. With the octyl and nonyl members, the dispersion curves exhibit a gradual change in shape on approaching and ultimately crossing the axis in the red end of the spectrum, and the condition corresponds closely to certain curves given by Lowry (J., 1915, **107**, 1200). His diagram shows the gradual change of the " complex but normal " to the " complex and anomalous " type on crossing the zero axis from the positive to the negative region of rotation. In the case of the two esters mentioned, the curves are complex, but do not show actual anomaly.

Actual anomaly is to be expected, but cannot probably be attained in this series owing to experimental difficulties. After reaching a maximum in the red end of the spectrum, the curves would have ultimately the zero axis as asymptote; on increasing the temperature, the axis would be crossed further to the left (octyl ester), and the maximum would move in the usual manner towards the violet. The high ratios in the violet, and the low ratios in the red for the hexyl and octyl esters are brought out particularly with increase of temperature, and show the combined effects of anomaly and low rotation value.

In the Patterson modification of the Armstrong diagram for the series of hexahydromandelic esters at various temperatures, the values obtained for particular wave-lengths (taking rotations for $\lambda_{5461}$ along the horizontal reference line) roughly lie on straight lines. These lines produced to the right intersect the reference line about the region + 7·5° (compare Patterson, J., 1916, **109**, 1181) for the lævo-esters. The diagram shows clearly that the "rational dispersion ratio" for any two wave-lengths is approximately constant for the homologous series under the temperature conditions described, that is, change of constitution (by increasing the length of the carbon chain) and increase of temperature are similar in effect.

The values of the molecular rotations for the *l*-lactates in a similar diagram lie practically on straight lines for particular wave-lengths. The lines converge in this case towards the left, intersecting the axis in the neighbourhood of + 2·2°. The angle made between the reference line and the line for any wave-length is slightly greater (especially for short wave-lengths) in the case of the hexahydromandelates than the corresponding angle in the case of the lactates. The tangents of the angles between the lines λ 5461 and λ 6708, 6152, 4861 for the former are, respectively, 0·343, 0·234, 0·335, and for the latter are 0·349, 0·223, and 0·300. In both cases increasing temperature or lengthening of the carbon chain produces a movement along the lines towards the right, except in certain lactates where maxima occur in the temperature–rotation curves.

The diagram correlates phenomena in both ester series and shows that, whilst the rotation is largely affected, molecular dispersion is little changed by substitution of the methyl for the *cyclo*hexyl group.

Whilst only an approximation for the esters, the diagram applies best to molecular, and not to specific rotation. The molecular dispersion is shown thereby to be chiefly dependent on the groups immediately surrounding the asymmetric centre, temperature and lengthening of the chain producing only secondary effects.

*Effect of Temperature.*

Increase of temperature causes a decrease in rotation. It is notable that in the case of the lactates increase in temperature causes an increase in rotation. In both cases, the temperature coefficient of change of rotation is greater the smaller the wave-length of light used, and it is decidedly greater for the hexahydromandelates than for the lactates. The temperature–rotation curves for light of different wave-lengths for the former series are lines of small curvature, convergent with increase of temperature (the lactates show a divergence), and inclined at an angle to the axis of zero rotation. The general direction tends to become more parallel to this axis for the higher esters, the curves of two of these, the octyl and nonyl, cutting the axis. No maxima or minima occur in the temperature range considered.

TABLE II.

*Molecular Rotatory Power.**

| Alkyl Ester. | λ 6708. | 6563. | 5893. | 5086. | 4455. | 4359. |
|---|---|---|---|---|---|---|
| | $[M]_\lambda^{30°}$. Temp. 30°. | | | | | |
| Methyl ..... | 25·7° | 28·2° | 36·8° | 54·4° | 73·7° | 77·6° |
| Ethyl ..... | 17·4 | 18·2 | 24·4 | 37·7 | 57·3 | 60·6 |
| Propyl ..... | 10·6 | 11·3 | 15·5 | 25·7 | 39·1 | 41·4 |
| Butyl ..... | 10·2 | 10·8 | 15·4 | 24·5 | 37·3 | 39·7 |
| Amyl ..... | 6·2 | 6·6 | 9·7 | 17·5 | 28·9 | 30·7 |
| Hexyl ..... | 5·7 | 6·2 | 9·3 | 17·5 | 27·2 | 28·7 |
| Heptyl ..... | 6·2 | 6·3 | 9·1 | 16·2 | 26·9 | 28·9 |
| Octyl ..... | 4·3 | 4·8 | 8·2 | 15·0 | 25·4 | 27·1 |
| Nonyl ..... | 5·0 | 5·5 | 8·3 | 15·9 | 24·9 | 26·4 |
| | $[M]_\lambda^{140°}$. Temp. 140°. | | | | | |
| Methyl ..... | 19·6 | 20·3 | 26·3 | 40·7 | 56·1 | 58·9 |
| Ethyl ..... | 10·0 | 10·4 | 14·5 | 22·6 | 33·2 | 35·6 |
| Propyl ..... | 4·9 | 5·4 | 8·3 | 15·7 | 27·1 | 29·0 |
| Butyl ..... | 4·8 | 5·3 | 7·8 | 14·2 | 22·1 | 23·3 |
| Amyl ..... | 3·1 | 3·3 | 4·9 | 10·2 | 17·3 | 18·9 |
| Hexyl ..... | 0·9 | 1·3 | 2·9 | 7·7 | 14·2 | 15·3 |
| Heptyl ..... | 1·3 | 1·6 | 3·6 | 8·1 | 13·9 | 14·9 |
| Octyl ..... | 0·4 | 0·6 | 2·4 | 7·6 | 14·7 | 16·2 |
| Nonyl ..... | 1·4 | 1·6 | 3·2 | 7·6 | 12·2 | 13·1 |

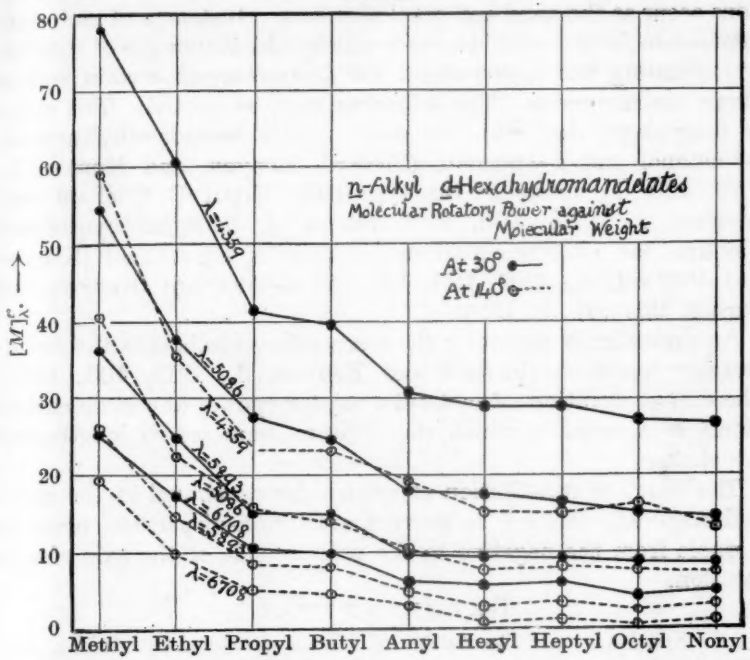
* Numerical values only.

The curves (Fig. 2) are obtained by interpolation of the molecular rotation–temperature curves for the wave-lengths in the above table. In general, the rotation decreases on ascending the homologous series; the curves gradually converge, approach and tend to become parallel to the axis of zero rotation. This means that the molecular rotation approaches a constant value for those esters investigated above the amyl ester. It is to be noticed that there

is a marked irregularity at the butyl ester, and a slight deviation in the form of the curve, especially for light of short wave-length, at the octyl ester, which may be due to the ester approaching the anomalous condition.

Comparison of our results with those for the esters derived from *l-iso*pulegol (Pickard, Hunter, Lewcock, and Pennington, J., 1920, **117**, 1248) shows that the elevation of molecular rotation occurs in the latter case at the *n*-valerate of *iso*pulegol, which corresponds in the chain to the *n*-butyl ester of hexahydromandelic acid.

FIG. 2.




On ascending the *n*-alkyl series, the negative rotation shown by the *l*-hexahydromandelic esters is reduced, the positive rotation shown by the *l*-lactates is increased; the movement in rotation due to the lengthening alkyl chain is in the same direction in each case. Again, in the higher members of these series, as in many others investigated (Pickard and Kenyon, J., 1914, **105**, 830; Phillips, J., 1923, **123**, 23, etc.), advance from one member to the next produces little change in molecular rotation. This is to be expected if Rule's suggestion (this vol., p. 1121) that " the influence of a substituent on the optical rotation of a parent compound is dependent in sign and magnitude on the change in electrostatic

moment" is correct. The difference in electrostatic moment at the asymmetric centre would become progressively smaller from one member to the next on lengthening the chain, but the electrostatic moment, *pari passu*, would increase (compare Thomson, *Phil. Mag.*, 1923, [vi], **46**, 497) except when the helical chain returns upon itself; here a depression in molecular rotation (when the rotation increases up the series), or an elevation (when the rotation decreases up the series), is to be expected, and not *vice versa*. In accordance with this, an elevation is shown by the *l*-hexahydromandelic series, and depressions by the *l*-lactates; in the former case, the elevation occurs at the butyl ester, in the latter, depressions occur at the amyl and octyl members. Instances of molecular rotation–molecular weight curves which exhibit increase of rotation on ascending the series and show *depressions* at certain carbon atoms are numerous. The following may be quoted. The esters of *l-iso*pulegol (*loc. cit.*), the *n*-esters of *d*-benzylmethylcarbinol, *d*-β-octanol and *d*-γ-nonanol (Pickard, Kenyon, and Hunter, J., 1923, **123**, 1), esters of the type $CH_3$·CH(OH)·R (Pickard and Kenyon, J., 1914, **105**, 830), ethers of benzylmethylcarbinol (Phillips, *loc. cit.*), the *n*-aliphatic ethers of *d*-β-octanol (Kenyon and McNicol, J., 1923, **123**, 14), and *d*-γ-nonanol (Kenyon and Barnes, this vol., p. 1395).

An exception is shown by the *n*-secondary alcohols in the homogeneous condition (Pickard and Kenyon, J., 1913, **103**, 1923). These show elevations of molecular rotatory power at certain carbon atoms in a series in which the rotation increases on lengthening the chain.

The effect of substitution of methyl for *cyclo*hexyl in the hexahydromandelic series is to move the rotation–dispersion curves as a whole from the negative to the positive side of the axis of zero rotation.

## Experimental.

### *Synthesis and Resolution of Hexahydromandelic Acid.*

Zelinsky (*Ber.*, 1908, **41**, 2677) described as the acid a compound which appears to have been the amide. The yield obtained by his method, however, was too poor for our requirements, hence *cyclo*hexyl bromide was changed directly to hexahydrobenzaldehyde, which gave through the cyanohydrin a satisfactory yield of the acid.

Ethyl orthoformate was prepared by the authors' method (*J. Soc. Chem. Ind.*, 1923, **42**, 429T).

Esterification of *cyclo*hexanol by the use of 48% hydrobromic acid (Scott, J., 1900, **77**, 648) having proved unsatisfactory (the crude products showed unsaturation, and the best yield obtained was 57%), *cyclo*hexyl bromide was prepared by Kohler and

Burnley's modification (*J. Amer. Chem. Soc.*, 1910, **43**, 412) of Freundler and Damond's method (*Compt. rend.*, 1905, **141**, 593).

With mechanical stirring, 148 g. of *cyclo*hexanol (b. p. 75°/20 mm.) were allowed to fall (1 drop in 2 secs.) into 152 g. (15% excess) of phosphorus tribromide below 0°. The product was left in the freezing mixture over-night, kept for 2 days at the ordinary temperature, and then poured on ice. After purification by Kohler and Burnley's method (*loc. cit.*), the bromide had b. p. 61—62°/20 mm. (yield 207 g.; 86%). It is important that no excess of *cyclo*hexanol be used, otherwise unsaturated products result. Efficient stirring during addition of the alcohol to the bromide raised the yield from 69 to 86%.

The yields of hexahydrobenzaldehyde obtained by the methods of Sabatier and Mailhe (*Compt. rend.*, 1904, **139**, 343), Bouveault (*Bull. Soc. chim.*, 1903, [iii], **29**, 1049), Zelinsky and Gutt (*Ber.*, 1907, **40**, 3051), and Wallach (*Annalen*, 1906, **347**, 316) are poor. Details of the method adopted by us are given (*J. Soc. Chem. Ind.*, 1923, **42**, 429T). The aldehyde is a colourless oil, b. p. 159·3°. Bouveault (*loc. cit.*) gives b. p. 159°.

*Preparation of Hexahydromandelonitrile and its Hydrolysis.*—Hexahydrobenzaldehyde bisulphite compound (100 g.) was well shaken with a saturated solution of 42 g. of potassium cyanide, and the nitrile was extracted with small portions of ether, the product being at the same time gradually diluted with water. The nitrile was heated under reflux for 1 hour with concentrated hydrochloric acid (*d* 1·16; 4 vols.). The nitrile remaining unchanged was separated while hot and again hydrolysed for 1 hour with fresh acid. This process was repeated, but complete hydrolysis was never attained, owing to the formation of *iso*nitrile. The nitrile should be hydrolysed immediately after its formation. Yield of acid 34·5 g. (47%); m. p. 134·7° (corr.).

The acid thus obtained was very soluble in hot water or ether, did not crystallise well from acetone, was moderately soluble in alcohol or benzene, and contained no water of crystallisation. The acid obtained by Zelinsky had m. p. about 166°, was readily soluble in hot water, from which it was obtained in silvery scales, difficultly soluble in ether, and crystallised well from acetone [Found by authors: C = 60·85; H = 8·83. Zelinsky found C = 60·64; H = 9·10. $C_8H_{14}O_3$ requires C = 60·72; H = 8·91%. Equiv. wt. = 157·6 (by silver salt), 157·8 (by titration). Calc., 158·1].

*Hexahydromandelamide* was isolated in quantity after a certain hydrolysis of hexahydrobenzaldehydecyanohydrin with concentrated hydrochloric acid. The product, after treatment with dilute caustic potash in the cold, gave m. p. 164°, crystallised from benzene

in a different manner from the acid, and when recrystallised from water had m. p. 165·2° (corr.). It was readily soluble in hot water or alcohol (from the former it was obtained in scales on cooling), difficultly soluble in ether or ligroin, and might be recrystallised from acetone (Found: N = 9·11. $C_8H_{15}O_2N$ requires N = 8·92%). The above properties correspond to those given by Zelinsky for the acid.

If the ethereal solution of the cyanohydrin be hydrolysed, the hydrolysis to the acid is not complete, and a quantity of hexahydromandelamide results. Zelinsky did not state that the nitrile was isolated from ethereal solution before hydrolysis. The best conditions for hydrolysis to the acid are, isolation of the cyanohydrin as rapidly as possible and hydrolysis for the time stated, otherwise a mixed product results.

*Resolution of Hexahydromandelic Acid.*—Complete resolution of the acid into the optically active enantiomorphs was effected by the use of quinine and morphine. A good criterion of optical purity was given by the fairly high value of the rotation of the methyl ester derived from both forms. Further evidence of completeness of resolution was obtained from the rotation of esters other than the methyl, of both forms of the acid, and of the dextro- and lævo-ammonium salts. The outline of the methods of resolution adopted is similar to that for the resolution of lactic acid by morphine (Wood, Such, and Scarf, *loc. cit.*).

*Isolation of optically pure dextro acid.* Hexahydromandelic acid (20 g.), exactly neutralised with *N*-potassium hydroxide, was added to 20 g. of the acid in 3000 c.c. of hot water containing 41 g. of quinine. The quantity of quinine added was sufficient to give the basic salt; the normal salt crystallises with difficulty. The whole was brought gradually to the boiling point; a quantity of the dark-coloured, syrupy quinine salt remained undissolved, which became solid on cooling. The solution was left over-night in ice, the mass of long, colourless needles separated, the liquid again brought to the boiling point in contact with the quinine salt, and a further crop of crystals obtained. This process was repeated eight times. Crystallisation took place below 45°, and was assisted by inoculation. The quinine salt was recrystallised twice, from 4000 c.c. and 3000 c.c., respectively, of water. To the hot solution was added excess of dilute ammonia, the precipitated quinine separated, and the solution reduced to 250 c.c. and rendered just alkaline with ammonia. Traces of quinine were separated, and the acid was obtained from the ammonium *d*-hexahydromandelate by acidification with dilute hydrochloric acid, filtration, and ether-extraction. The acid was purified by redissolving in warm water,

leaving until cold, extracting the supersaturated solution with ether, and crystallising from ether. The resolution gave 58% of the theoretical quantity of *d*-acid.

Recovery of the partly resolved hexahydromandelic acid from the mother-liquors was effected by addition of excess of dilute ammonia, filtration, reduction in volume to 300 c.c., further addition of ammonia until just alkaline, and further procedure as detailed above. Resolution by means of quinine proved more difficult than by the use of morphine.

*d*-Hexahydromandelic acid crystallises from ether in prisms which appear to be monoclinic, m. p. 129·7° (corr.); $[\alpha]_D^{25°} = +13·51°$ ($\alpha = +1·68°$ for 0·8570 g. of acid in 6·9 c.c. of solution in absolute alcohol).

Quinine *d*-hexahydromandelate crystallises from water in long needles, m. p. 45°; $[\alpha]_D^{25°} = -123·24°$ ($\alpha = -5·21°$ for 0·4366 g. of salt in 10·3 c.c. of solution in absolute alcohol).

Ammonium *d*-hexahydromandelate is of little value as a criterion of the optical purity of the acid, owing to its small rotatory power: $[\alpha]_D^{24°} = -7·78°$ ($\alpha = -0·56°$ for 0·5 g. of acid and 2·0 c.c. of ammonium hydroxide, *d* 0·88, made up to 7·7 c.c. of solution with distilled water). The rotations of the sodium and potassium salts also are of opposite sign to that of the acid.

*Isolation of optically pure lævo-acid* by means of morphine was carried out as follows: Half the available acid (27 g.) was neutralised by *N*-potassium hydroxide solution, and the other half by the equivalent quantity (51·8 g.) of morphine in 900 c.c. of boiling water. The solutions were mixed, cooled, and crystals of morphine *l*-hexahydromandelate were precipitated. On evaporation to half volume, an additional crop was obtained. The morphine salt was recrystallised twice from water, the rotation then being constant. To the boiling solution (900 c.c.) of the salt, ammonia was added, and the morphine filtered off. The solution, kept just alkaline with ammonia, was reduced in volume to 250 c.c. and left overnight. The small quantity of precipitated morphine was separated, and the *l*-hexahydromandelic acid isolated by acidification of the solution of its ammonium salt in a similar manner to that for the dextro-acid. The resolution gave 85% of the theoretical quantity of *l*-acid.

The mother-liquors were worked up to obtain partly resolved *d*-acid, for resolution with quinine.

*l*-Hexahydromandelic acid crystallises from ether in hexagonal clusters, m. p. 129·7° (identical with that of the dextro-enantiomorph); $[\alpha]_D^{23°} = -13·62°$ ($\alpha = -1·04°$ for 0·5047 g. of the acid in 6·6 c.c. of solution in absolute alcohol).

Morphine *l*-hexahydromandelate crystallises from water in short needles, m. p. 127·6° (decomp.); $[\alpha]_D^{25°} = -63·73°$ ($\alpha = -3·51°$ for 0·6392 g. in 11·6 c.c. of solution in absolute alcohol). The rotation of the salt was constant after the second recrystallisation.

Ammonium *l*-hexahydromandelate gave $[\alpha]_D^{24°} = +7·51°$ ($\alpha = +0·54°$; 0·50 g. of acid, 2 c.c. ammonium hydroxide, *d* 0·88, made up to 7·7 c.c. of solution with water).

*Resolution by strychnine and brucine.* Both alkaloids gave as the less soluble salts in water and acetone, those derived from the dextro-acid. The partly resolved strychnine salt is precipitated from water as a syrup. The brucine salt is similar, but it may with difficulty be crystallised from acetone as extremely deliquescent feathery needles. After three recrystallisations from acetone, the acid derived from this salt was not completely resolved.

*Methyl* l-*Hexahydromandelate.*—In general, esterification without racemisation can be effected by both the sulphuric and hydrochloric acid methods, but the higher-boiling fraction of esters produced by the latter method frequently showed an elevation of rotation which probably indicated lactide formation.

Kahlbaum's methyl alcohol (4 mols.; 6·2 g., dried with anhydrous sodium sulphate) was mixed with 1·5 g. of concentrated sulphuric acid, cooled, and 7·5 g. of *l*-hexahydromandelic acid were added; the mixture was heated on the water-bath at 65—70° for 2½ hours, and allowed to cool. The excess of sulphuric acid was removed by dilution with dry ether (4 vols.), addition of potassium carbonate, filtration from the salts, and removal of the ether.

After four distillations in a vacuum, the ester had b. p. 108·7°/5 mm. (oil-bath temperature 143°) and m. p. +4·7°. Yield 6·5 g. (80%). The ester gave rotation $\alpha_D^{24°} = -23·00°$. A fifth distillation caused no change in rotation. Since the specific rotation of this ester was much higher than that of the *n*-propyl ester, two further specimens of the acid, dextro- and lævo-rotatory respectively, were esterified by the sulphuric and hydrochloric acid methods.

(1) Methyl *d*-hexahydromandelate was prepared by adding 5·0 g. of the *d*-acid to a mixture of 4·1 g. of methyl alcohol and 1·5 g. of concentrated sulphuric acid. The mixture was heated at 65—70° for 3 hours. The ester, isolated as in the above preparation, had b. p. 110·4—110·9°/7 mm. (oil-bath temperature 150°) and $\alpha_D^{25°} + 23·11°$.

(2) Methyl *l*-hexahydromandelate was prepared by passing 0·258 g. (6%) of dry gaseous hydrogen chloride into a mixture of 5 g. of *l*-hexahydromandelic acid and 4·1 g. of methyl alcohol, and heating at 65° for 2½ hours. The ester, treated as in the above

preparations, had b. p. 116·5°/12 mm. (oil-bath temperature 138°). After four distillations, it gave rotation $\alpha_D^{25°} = -23·01°$.

The ester exhibits complex rotatory dispersion.

Densities $d_4^t$ determined: 1·0992 at −14·6°; 1·0698 at +17·6° 1·0313 at 60·3°; 1·0081 at 85·9°; 0·9686 at 128·7°.

| | $d_4^{-12°}$ 1·0970. | $d_4^{19·6°}$ 1·0683. | $d_4^{62°}$ 1·0296. | $d_4^{105°}$ 0·9906. | $d_4^{123°}$ 0·9743. | $d_4^{158·5°}$ 0·9596. |
|---|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{-12°}$. | $[\alpha]_\lambda^{19·6°}$. | $[\alpha]_\lambda^{62°}$. | $[\alpha]_\lambda^{105°}$. | $[\alpha]_\lambda^{123°}$. | $[\alpha]_\lambda^{158·5°}$. |
| 6708 ..... | −17·10° | −15·80° | −14·72° | −13·08° | −12·17° | −10·54° |
| 6563 ..... | 17·60 | 16·70 | 15·38 | 13·49 | 12·71 | 10·93 |
| 6152 ..... | 20·59 | 19·69 | 18·03 | 15·88 | 14·80 | 12·67 |
| 5893 ..... | 23·04 | 21·95 | 19·94 | 17·62 | 16·45 | 14·07 |
| 5461 ..... | 28·49 | 26·69 | 24·32 | 21·49 | 20·17 | 17·74 |
| 5324 ..... | 30·33 | 28·65 | 25·89 | 23·05 | 21·79 | 19·27 |
| 5086 ..... | 34·32 | 32·29 | 29·26 | 26·29 | 24·88 | 22·24 |
| 4861 ..... | 38·31 | 36·18 | 32·97 | 29·59 | 28·15 | 25·20 |
| 4455 ..... | 46·38 | 43·79 | 40·07 | 36·20 | 34·39 | 30·56 |
| 4359 ..... | 48·49 | 45·95 | 42·26 | 38·06 | 36·11 | 32·18 |

$a_\lambda^{-12°} = [a]_\lambda^{-12°} \times 1·0970$; $a_\lambda^{19·6°} = [a]_\lambda^{19·6°} \times 1·0683$; $a_\lambda^{62°} = [a]_\lambda^{62°} \times 1·0296$; $a_\lambda^{105°} = [a]_\lambda^{105°} \times 0·9906$; $a_\lambda^{123°} = [a]_\lambda^{123°} \times 0·9743$; $a_\lambda^{158·5°} = [a]_\lambda^{158·5°} \times 0·960$. $[M]_\lambda^t = [a]_\lambda^t \times 1·72$.

*Ethyl* l-*Hexahydromandelate*.—The ester was prepared by heating 7·0 g. of *l*-hexahydromandelic acid with a mixture of ethyl alcohol (8·2 g.) and concentrated sulphuric acid (2·17 g.) for 3 hours at 60—65°. The product was treated in the same manner as the methyl ester.

After three distillations in a vacuum, the ester formed a mass of needles, m. p. 43·1° (corr.), b. p. 133°/20 mm. Yield 6·4 g. (78%). The ester exhibits complex rotatory dispersion.

Densities $d_4^t$ determined: 1·0160 at 39·3°; 0·9868 at 73·1° 0·9677 at 94·6°; 0·9293 at 138·9°; 0·9048 at 167·3°.

| | $d_4^{26·5°}$ 1·0268. | $d_4^{63·1°}$ 0·9952. | $d_4^{89·3°}$ 0·9724. | $d_4^{123°}$ 0·9426. | $d_4^{152·1°}$ 0·9176. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{26·5°}$. | $[\alpha]_\lambda^{63·1°}$. | $[\alpha]_\lambda^{89·3°}$. | $[\alpha]_\lambda^{123°}$. | $[\alpha]_\lambda^{152·1°}$. |
| 6708 ..... | −9·52° | −7·87° | −6·69° | −5·59° | −5·20° |
| 6563 ..... | 10·00 | 8·21 | 7·03 | 5·85 | 5·42 |
| 6152 ..... | 11·71 | 9·77 | 8·54 | 7·35 | 6·55 |
| 5893 ..... | 13·34 | 11·08 | 9·84 | 8·43 | 7·40 |
| 5461 ..... | 16·40 | 13·79 | 12·20 | 10·43 | 9·14 |
| 5324 ..... | 17·97 | 15·10 | 13·24 | 11·32 | 9·95 |
| 5086 ..... | 20·64 | 17·42 | 15·45 | 13·19 | 11·53 |
| 4861 ..... | 23·90 | 19·93 | 17·51 | 14·93 | 12·98 |
| 4455 ..... | 31·32 | 25·96 | 22·73 | 19·24 | 16·80 |
| 4359 ..... | 33·31 | 27·97 | 24·51 | 20·71 | 18·01 |

$a_\lambda^{26·5°} = [a]_\lambda^{26·5°} \times 1·027$; $a_\lambda^{63·1°} = [a]_\lambda^{63·1°} \times 0·9952$; $a_\lambda^{89·3°} = [a]_\lambda^{89·3°} \times 0·9724$; $a_\lambda^{123°} = [a]_\lambda^{123°} \times 0·9426$; $a_\lambda^{152·1°} = [a]_\lambda^{152·1°} \times 0·9176$. $[M]_\lambda^t = [a]_\lambda^t \times 1·86$.

n-*Propyl Hexahydromandelate*.—Since the methyl ester showed unusual properties in the lactate series (Wood, Such, and Scarf,

*loc. cit.*), methods of esterification were investigated in the preparation of the propyl ester. Three specimens of the ester prepared as below were examined.

(1) The ester prepared from the *l*-acid by the hydrogen chloride method (described under the methyl ester) had rotation $\alpha_D^{22^\circ} = -8{\cdot}31^\circ$.

(2) A specimen of the *d*-ester prepared by the use of 12·9% hydrogen chloride under similar conditions to those of the last experiment had rotation $\alpha_D^{22^\circ} = +13{\cdot}06^\circ$ after the first fractional distillation; this probably indicated lactide or anhydride formation. After five distillations, the ester had b. p. 129·5—130·0°/5 mm. (oil-bath temperature 162°), and gave constant rotation $\alpha_D^{22^\circ} = +8{\cdot}40^\circ$.

(3) To a cold mixture of 7·8 g. of propyl alcohol and 1·5 g. (sufficient to form dihydrated sulphuric acid with the water produced) of concentrated sulphuric acid, 5·07 g. of *l*-hexahydromandelic acid were added. The solution was heated for 3 hours at 60°, cooled, and subsequently treated as for the methyl ester. Yield 4·8 g. (73%). After four vacuum distillations, the ester had b. p. 130·0°/5 mm. (oil-bath temp. 155°), m. p. 4·6°, and gave rotation $\alpha_D^{19^\circ} = -8{\cdot}35^\circ$.

The ester exhibits complex rotatory dispersion.

Densities $d_4^t$ determined: 1·0334 at 0·0°; 1·0038 at 34·9°; 0·9776 at 64·6°; 0·9433 at 103·7°; 0·9257 at 124·5°; 0·9015 at 152·2°.

| | $d_4^{2\cdot5^\circ}$ 1·0312. | $d_4^{19^\circ}$ 1·0170. | $d_4^{48\cdot2^\circ}$ 0·9918. | $d_4^{68\cdot8^\circ}$ 0·9739. | $d_4^{96^\circ}$ 0·9500. | $d_4^{146\cdot4^\circ}$ 0·9065. |
|---|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{2\cdot5^\circ}$. | $[\alpha]_\lambda^{19^\circ}$. | $[\alpha]_\lambda^{48\cdot2^\circ}$. | $[\alpha]_\lambda^{68\cdot8^\circ}$. | $[\alpha]_\lambda^{96^\circ}$. | $[\alpha]_\lambda^{146\cdot4^\circ}$. |
| 6708 ..... | −6·12° | −5·58° | −4·79° | −4·12° | −3·46° | −2·36° |
| 6563 ..... | 6·53 | 5·91 | 5·09 | 4·36 | 3·67 | 2·54 |
| 6152 ..... | 7·77 | 7·19 | 6·18 | 5·43 | 4·60 | 3·33 |
| 5893 ..... | 8·87 | 8·22 | 7·09 | 6·27 | 5·29 | 4·03 |
| 5461 ..... | 11·69 | 10·63 | 9·37 | 8·39 | 7·19 | 5·75 |
| 5324 ..... | 12·53 | 11·57 | 10·16 | 9·13 | 7·80 | 6·23 |
| 5086 ..... | 14·55 | 13·24 | 11·90 | 10·70 | 9·25 | 7·71 |
| 4861 ..... | 16·87 | 15·67 | 13·75 | 12·61 | 11·05 | 9·48 |
| 4455 ..... | 21·77 | 20·42 | 18·22 | 16·91 | 15·29 | 13·30 |
| 4359 ..... | 23·29 | 21·60 | 19·19 | 17·89 | 16·28 | 14·26 |

$\alpha_\lambda^{2\cdot5^\circ} = [\alpha]_\lambda^{2\cdot5^\circ} \times 1{\cdot}031$; $\alpha_\lambda^{19^\circ} = [\alpha]_\lambda^{19^\circ} \times 1{\cdot}017$; $\alpha_\lambda^{48\cdot2^\circ} = [\alpha]_\lambda^{48\cdot2^\circ} \times 0{\cdot}9918$; $\alpha_\lambda^{68\cdot8^\circ} = [\alpha]_\lambda^{68\cdot8^\circ} \times 0{\cdot}9739$; $\alpha_\lambda^{96^\circ} = [\alpha]_\lambda^{96^\circ} \times 0{\cdot}95$; $\alpha_\lambda^{146\cdot4^\circ} = [\alpha]_\lambda^{146\cdot4^\circ} \times 0{\cdot}9065$.
$[M]_\lambda^t = [\alpha]_\lambda^t \times 2$.

n-*Butyl* l-*Hexahydromandelate*.—The ester was prepared by the sulphuric acid method, using 4 mols. of *n*-butyl alcohol, and sufficient sulphuric acid to form the dihydrated acid with the water formed. The solution was warmed at 70—75° for 3½ hours. The purified ester was a colourless oil, b. p. 147°/11 mm. (oil-bath temperature 175°) and m. p. −0·7°.

Densities $d_{4^\circ}^{t^\circ}$ determined: 1·0213 at − 8·0°; 1·0118 at + 4·3°; 0·9841 at 38·3°; 0·9357 at 97·4°; 0·8956 at 147·0°.

| | $d_{4^\circ}^{-6\cdot5^\circ}$ 1·0203. | $d_{4^\circ}^{14^\circ}$ 1·0038. | $d_{4^\circ}^{50\cdot7^\circ}$ 0·9742. | $d_{4^\circ}^{85\cdot3^\circ}$ 0·9459. | $d_{4^\circ}^{152^\circ}$ 0·8915. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{-6\cdot5^\circ}$. | $[\alpha]_\lambda^{14^\circ}$. | $[\alpha]_\lambda^{50\cdot7^\circ}$. | $[\alpha]_\lambda^{85\cdot3^\circ}$. | $[\alpha]_\lambda^{152^\circ}$. |
| 6708 ..... | −6·04° | −5·27° | −4·06° | −3·24° | −2·10° |
| 6563 ..... | 6·42 | 5·66 | 4·37 | 3·49 | 2·25 |
| 6152 ..... | 7·90 | 6·82 | 5·38 | 4·34 | 2·82 |
| 5893 ..... | 8·69 | 7·94 | 6·31 | 5·08 | 3·36 |
| 5461 ..... | 11·04 | 9·88 | 7·99 | 6·62 | 4·72 |
| 5324 ..... | 11·94 | 10·76 | 8·74 | 7·27 | 5·31 |
| 5086 ..... | 13·94 | 12·47 | 10·62 | 8·48 | 6·27 |
| 4861 ..... | 15·93 | 14·51 | 12·09 | 10·04 | 7·48 |
| 4455 ..... | 20·53 | 18·74 | 15·93 | 13·28 | 9·78 |
| 4359 ..... | 21·83 | 19·91 | 16·93 | 14·31 | 10·36 |

$a_\lambda^{-6\cdot5^\circ} = [\alpha]_\lambda^{-6\cdot5^\circ} \times 1\cdot0203$; $a_\lambda^{14^\circ} = [\alpha]_\lambda^{14^\circ} \times 1\cdot0038$; $a_\lambda^{50\cdot7^\circ} = [\alpha]_\lambda^{50\cdot7^\circ} \times 0\cdot9742$; $a_\lambda^{85\cdot3^\circ} = [\alpha]_\lambda^{85\cdot3^\circ} \times 0\cdot9459$; $a_\lambda^{152^\circ} = [\alpha]_\lambda^{152^\circ} \times 0\cdot8915$. $[M]_\lambda^{t^\circ} = [\alpha]_\lambda^{t^\circ} \times 2\cdot14$.

n-*Amyl* d-*hexahydromandelate* was prepared, under similar conditions to those employed for the butyl ester, from Kahlbaum's *n*-amyl alcohol, and had b. p. 164·5°/12 mm. (oil-bath temperature 204°); it crystallised, on cooling, in small clusters of prisms, m. p. − 2·5°. After a fourth distillation, the rotation was unchanged. Complex rotatory dispersion is exhibited by this ester.

Densities $d_{4^\circ}^{t^\circ}$ determined: 1·0135 at − 8·0°; 0·9926 at + 16·6°; 0·9640 at 51·3°; 0·9133 at 114·6°; 0·8745 at 159·1°.

| | $d_{4^\circ}^{5\cdot3^\circ}$ 1·0111. | $d_{4^\circ}^{23^\circ}$ 0·9873. | $d_{4^\circ}^{67\cdot1^\circ}$ 0·9508. | $d_{4^\circ}^{118^\circ}$ 0·9088. | $d_{4^\circ}^{156\cdot8^\circ}$ 0·8767. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{5\cdot3^\circ}$. | $[\alpha]_\lambda^{23^\circ}$. | $[\alpha]_\lambda^{67\cdot1^\circ}$. | $[\alpha]_\lambda^{118^\circ}$. | $[\alpha]_\lambda^{156\cdot8^\circ}$. |
| 6708 ..... | +3·14° | +2·80° | +2·24° | +1·60° | +1·15° |
| 6563 ..... | 3·38 | 2·99 | 2·37 | 1·66 | 1·21 |
| 6152 ..... | 4·25 | 3·69 | 2·99 | 2·16 | 1·53 |
| 5893 ..... | 5·01 | 4·43 | 3·51 | 2·54 | 1·89 |
| 5461 ..... | 6·73 | 6·01 | 4·86 | 3·65 | 2·90 |
| 5324 ..... | 7·36 | 6·61 | 5·48 | 4·14 | 3·32 |
| 5086 ..... | 8·83 | 7·94 | 6·51 | 5·02 | 4·07 |
| 4861 ..... | 10·58 | 9·54 | 7·78 | 6·05 | 5·08 |
| 4455 ..... | 14·85 | 13·06 | 10·67 | 8·43 | 7·00 |
| 4359 ..... | 16·07 | 14·01 | 11·46 | 9·13 | 7·64 |

$a_\lambda^{5\cdot3^\circ} = [\alpha]_\lambda^{5\cdot3^\circ} \times 1\cdot011$; $a_\lambda^{23^\circ} = [\alpha]_\lambda^{23^\circ} \times 0\cdot9873$; $a_\lambda^{67\cdot1^\circ} = [\alpha]_\lambda^{67\cdot1^\circ} \times 0\cdot951$; $a_\lambda^{118^\circ} = [\alpha]_\lambda^{118^\circ} \times 0\cdot9088$; $a_\lambda^{156\cdot8^\circ} = [\alpha]_\lambda^{156\cdot8^\circ} \times 0\cdot8767$. $[M]_\lambda^{t^\circ} = [\alpha]_\lambda^{t^\circ} \times 2\cdot28$.

n-*Hexyl* l-*hexahydromandelate* was prepared by the sulphuric acid method from *n*-hexyl alcohol, b. p. 157·0°/760 mm.; the latter was prepared from pure *n*-amyl alcohol by the cyanide synthesis (J., 1923, **123**, 600). The ester boiled at 160·5°/7 mm. (oil-bath temperature 190°) and melted sharply at − 1·5°. Complex rotatory dispersion is exhibited.

Densities $d_{4^\circ}^{t^\circ}$ determined: 1·0091 at − 12·0°; 0·9861 at + 14·3°; 0·9518 at 57·2°; 0·9136 at 101·3°; 0·8893 at 133·0°; 0·8704 at 154·6°.

| | $d_4^{6\cdot5°}$ 1·0045. | $d_4^{20\cdot7°}$ 0·9816. | $d_4^{85\cdot5°}$ 0·9278. | $d_4^{121\cdot6°}$ 0·8979. | $d_4^{147\cdot2°}$ 0·8768. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{6\cdot5°}$. | $[\alpha]_\lambda^{20\cdot7°}$. | $[\alpha]_\lambda^{85\cdot5°}$. | $[\alpha]_\lambda^{121\cdot6°}$. | $[\alpha]_\lambda^{147\cdot2°}$. |
| 6708 ..... | −3·05° | −2·59° | −1·29° | −0·71° | −0·30° |
| 6563 ..... | 3·26 | 2·79 | 1·47 | 0·85 | 0·46 |
| 6152 ..... | 4·03 | 3·51 | 2·00 | 1·29 | 0·80 |
| 5893 ..... | 4·69 | 4·15 | 2·52 | 1·67 | 1·01 |
| 5461 ..... | 6·44 | 5·72 | 3·86 | 2·45 | 1·78 |
| 5324 ..... | 7·08 | 6·33 | 4·37 | 2·89 | 2·12 |
| 5086 ..... | 8·32 | 7·48 | 5·40 | 3·92 | 2·83 |
| 4861 ..... | 9·64 | 8·69 | 6·48 | 4·87 | 3·58 |
| 4455 ..... | 12·67 | 11·61 | 8·77 | 6·92 | 5·42 |
| 4359 ..... | 13·16 | 12·13 | 9·33 | 7·43 | 5·83 |

$a_\lambda^{6\cdot5°} = [\alpha]_\lambda^{6\cdot5°} \times 1\cdot0045$; $a_\lambda^{20\cdot7°} = [\alpha]_\lambda^{20\cdot7°} \times 0\cdot9816$; $a_\lambda^{85\cdot5°} = [\alpha]_\lambda^{85\cdot5°} \times 0\cdot9278$; $a_\lambda^{121\cdot6°} = [\alpha]_\lambda^{121\cdot6°} \times 0\cdot8979$; $a_\gamma^{147\cdot2°} = [\alpha]_\lambda^{147\cdot2°} \times 0\cdot8768$. $[M]_\lambda^{t°} = [\alpha]_\lambda^{t°} \times 2\cdot42$.

n-*Heptyl* d-*hexahydromandelate* was prepared by the sulphuric acid method from *n*-heptyl alcohol, b. p. 174·6—174·9°/745 mm. The conditions were as described under the butyl ester. The ester had b. p. 182·5°/12 mm. (oil-bath temperature, 215°) and m. p. — 7·1°. It exhibited complex rotatory dispersion.

Densities $d_4^{t°}$ determined: 0·9952 at — 10·5°; 0·9780 at + 12·5°; 0·9351 at 66·8°; 0·8966 at 115·2°; 0·8563 at 165·5°.

| | $d_4^{1\cdot5°}$ 0·9867. | $d_4^{23\cdot1°}$ 0·9697. | $d_4^{65\cdot8°}$ 0·9360. | $d_4^{110\cdot3°}$ 0·9004. | $d_4^{162\cdot5°}$ 0·8586. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{1\cdot5°}$. | $[\alpha]_\lambda^{23\cdot1°}$. | $[\alpha]_\lambda^{65\cdot8°}$. | $[\alpha]_\lambda^{110\cdot3°}$. | $[\alpha]_\lambda^{162\cdot5°}$. |
| 6708 ..... | +3·04° | +2·58° | +1·67° | +0·98° | +0·19° |
| 6563 ..... | 3·19 | 2·72 | 1·80 | 1·11 | 0·30 |
| 6152 ..... | 3·74 | 3·20 | 2·29 | 1·55 | 0·79 |
| 5893 ..... | 4·33 | 3·74 | 2·71 | 1·98 | 1·07 |
| 5461 ..... | 5·69 | 5·02 | 3·78 | 2·82 | 1·75 |
| 5324 ..... | 6·25 | 5·54 | 4·22 | 3·22 | 2·00 |
| 5086 ..... | 7·34 | 6·61 | 5·16 | 3·95 | 2·61 |
| 4861 ..... | 8·75 | 7·81 | 6·23 | 4·79 | 3·19 |
| 4455 ..... | 11·92 | 10·85 | 8·71 | 6·75 | 4·53 |
| 4359 ..... | 12·89 | 11·68 | 9·50 | 7·32 | 4·84 |

$a_\lambda^{1\cdot5°} = [\alpha]_\lambda^{1\cdot5°} \times 0\cdot9867$; $a_\lambda^{23\cdot1°} = [\alpha]_\lambda^{23\cdot1°} \times 0\cdot9697$; $a_\lambda^{65\cdot8°} = [\alpha]_\lambda^{65\cdot8°} \times 0\cdot9360$; $a_\lambda^{110\cdot3°} = [\alpha]_\lambda^{110\cdot3°} \times 0\cdot9004$; $a_\lambda^{162\cdot5°} = [\alpha]_\lambda^{162\cdot5°} \times 0\cdot8586$. $[M]_\lambda^{t°} = [\alpha]_\lambda^{t°} \times 2\cdot56$.

The ester was found to be partly racemised after heating at 183° for 2 hours.

n-*Octyl* l-*hexahydromandelate* was prepared, under similar conditions to those employed for the heptyl ester (except that the time of heating was 4½ hours), from *n*-octyl alcohol, b. p. 195·5—195·8°/758 mm. After three fractional distillations, the ester had b. p. 184°/7 mm. (oil-bath temperature, 220°) and m. p. + 7·8°. Complex rotatory dispersion is exhibited, and the rotation–dispersion curves cross the axis of zero rotation at high temperatures and for light of long wave-length.

Densities $d_4^{t°}$ determined: 0·9861 at — 9·6°; 0·9738 at + 7·0°;

0·9421 at 48·9°; 0·8933 at 111·8°; 0·8584 at 156·9°; 0·8283 at 197·2°; 0·8240 at 203·1°.

| | $d_4^{7·6°}$ 0·9845. | $d_4^{23°}$ 0·9612. | $d_4^{86·1°}$ 0·9130. | $d_4^{147·5°}$ 0·8668. | $d_4^{199·3°}$ 0·8261. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{7·6°}$. | $[\alpha]_\lambda^{23°}$. | $[\alpha]_\lambda^{86·1°}$. | $[\alpha]_\lambda^{147·5°}$. | $[\alpha]_\lambda^{199·3°}$. |
| 6708 ..... | −1·98° | −1·62° | −0·83° | −0·02° | +0·99° |
| 6563 ..... | 2·25 | 1·89 | 1·05 | 0·11 | 0·89 |
| 6152 ..... | 3·01 | 2·56 | 1·57 | 0·51 | 0·73 |
| 5893 ..... | 3·63 | 3·08 | 1·97 | 0·71 | 0·53 |
| 5461 ..... | 4·80 | 4·19 | 2·98 | 1·57 | −0·15 |
| 5324 ..... | 5·29 | 4·61 | 3·35 | 1·92 | 0·41 |
| 5086 ..... | 6·37 | 5·75 | 4·28 | 2·61 | 0·80 |
| 4861 ..... | 7·47 | 6·77 | 5·22 | 3·42 | 1·23 |
| 4455 ..... | 10·34 | 9·54 | 7·74 | 5·09 | 1·89 |
| 4359 ..... | 11·05 | 10·22 | 8·34 | 5·62 | 2·35 |

$a_\lambda^{7·6°} = [\alpha]_\lambda^{7·6°} \times 0·9845$; $a_\lambda^{23°} = [\alpha]_\lambda^{23°} \times 0·9612$; $a_\lambda^{86·1°} = [\alpha]_\lambda^{86·1°} \times 0·9130$; $a_\lambda^{147·5°} = [\alpha]_\lambda^{147·5°} \times 0·8668$; $a_\lambda^{199·3°} = [\alpha]_\lambda^{199·3°} \times 0·8261$. $[M]_\lambda^{t°} = [\alpha]_\lambda^{t°} \times 2·7$.

n-*Nonyl* d-*hexahydromandelate* was prepared by the sulphuric acid method from *n*-nonyl alcohol, b. p. 213·1—213·4°/757 mm., obtained by the cyanide synthesis from *n*-octyl alcohol (see under *n*-hexyl *l*-hexahydromandelate). The time of heating at 65° was 5 hours. The ester had b. p. 193·3—194·5°/16 mm. (oil-bath temperature, 234°) and m. p. + 5·4°; it crystallised in short, colourless prisms. Complex rotatory dispersion is exhibited, and, similar to those for the octyl ester, the rotation–dispersion curves cross the axis of zero rotation at high temperatures for light of long wave-length.

Densities $d_4^{t°}$ determined: 0·9757 at − 5·5°; 0·9600 at + 14·7°; 0·9087 at 85·0°; 0·8791 at 121·3°; 0·8446 at 167·5°; 0·8192 at 201·5°.

| | $d_4^{3·4°}$ 0·9742. | $d_4^{22·5°}$ 0·9543. | $d_4^{66·6°}$ 0·9210. | $d_4^{132·4°}$ 0·8715. | $d_4^{201·8°}$ 0·8192. |
|---|---|---|---|---|---|
| λ. | $[\alpha]_\lambda^{3·4°}$. | $[\alpha]_\lambda^{22·5°}$. | $[\alpha]_\lambda^{66·6°}$. | $[\alpha]_\lambda^{132·4°}$. | $[\alpha]_\lambda^{201·8°}$. |
| 6708 ..... | +2·03° | +1·84° | +1·43° | +0·59° | −0·43° |
| 6563 ..... | 2·26 | 1·99 | 1·54 | 0·69 | 0·37 |
| 6152 ..... | 2·83 | 2·60 | 1·98 | 0·96 | −0·14 |
| 5893 ..... | 3·35 | 3·04 | 2·35 | 1·26 | +0·02 |
| 5461 ..... | 4·71 | 4·19 | 3·24 | 2·08 | 0·42 |
| 5324 ..... | 5·35 | 4·74 | 3·63 | 2·30 | 0·61 |
| 5086 ..... | 6·56 | 5·78 | 4·55 | 2·87 | 1·00 |
| 4861 ..... | 7·79 | 6·93 | 5·40 | 3·52 | 1·39 |
| 4455 ..... | 10·39 | 9·06 | 7·31 | 4·61 | 2·20 |
| 4359 ..... | 11·09 | 9·48 | 7·76 | 4·95 | 2·42 |

$a_\lambda^{3·4°} = [\alpha]_\lambda^{3·4°} \times 0·9742$; $a_\lambda^{22·5°} = [\alpha]_\lambda^{22·5°} \times 0·9543$; $a_\lambda^{66·6°} = [\alpha]_\lambda^{66·6°} \times 0·9210$; $a_\lambda^{132·4°} = [\alpha]_\lambda^{132·4°} \times 0·8715$; $a_\lambda^{201·8°} = [\alpha]_\lambda^{201·8°} \times 0·8192$. $[M]_\lambda^{t°} = [\alpha]_\lambda^{t°} \times 2·84$.

The rotations of the esters did not change on keeping; from this it was inferred that the tendency for lactide formation is small. Of the nine esters examined (methyl to *n*-nonyl), the five esters, methyl to *n*-amyl, have an apple-like odour. They are liquids at

the ordinary temperature, except the ethyl ester (m. p. 43·1°), and melt sharply within a few degrees of zero.

While the esters have the same sign of rotation as the acid from which they are derived, the sodium, potassium, and ammonium salts are of opposite sign.

*Summary.*

1. Hexahydromandelic acid has been synthesised from *cyclo*hexanol by means of the Grignard reagent, and resolved by the use of morphine and quinine.

2. In the homogeneous condition, the *n*-alkyl hexahydromandelates (methyl to *n*-nonyl inclusive) exhibit complex rotatory dispersion of a similar type. The rotation–dispersion curves for the octyl and nonyl members cross the axis of zero rotation, inferring an approach to anomaly.

3. The effect of substitution of the *cyclo*hexyl group for the methyl group of lactic acid is that the esters, generally, retain the sign of rotation of the acid from which they are derived, the molecular dispersion is slightly greater than for the lactates, and the rotatory power decreases with rise of temperature. Temperature has a greater effect on the rotation of the hexahydromandelates than on that of the lactates.

4. The molecular rotation appears to decrease to an approximately constant value on ascending the series. An elevation of rotation occurs at the *n*-butyl, and a deviation at the *n*-octyl ester. The latter may be due to anomaly.

5. Dispersion is due to the groups immediately surrounding the asymmetric centre, temperature and lengthening of the carbon chain producing secondary effects.

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EDGBASTON.

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## CCCLXII.—*Studies of Electrolytic Polarisation. Part II. The Cathodic Overvoltage of Mercury.*

By SAMUEL GLASSTONE.

THE polarisation of a mercury cathode in acid solution has already been studied by several authors; Tafel (*Z. physikal. Chem.*, 1905, **50**, 641) and Lewis and Jackson (*ibid.*, 1906, **56**, 193) have measured

overvoltages by the direct method; Dunnill (J., 1921, **119**, 1081) compared the direct and commutator methods, whilst Newbery (*ibid.*, 1922, **121**, 7) has described the effect of time, commutator velocity, and current density on the cathodic overvoltage of mercury in *N*-sulphuric acid. The last author defines overvoltage as "the reversible portion of the total back *E.M.F.* of an electrode," and concludes that "no approximation to the true overvoltage can be obtained without the use of a commutator" and that a close approximation is obtained "when the commutator speed is not less than 1500 revs. per minute."

As a result of previous investigations on the lead electrode (*ibid.*, 1924, **125**, 250), the present author has shown that the apparently constant back *E.M.F.*'s obtained with the commutator revolving at high speeds may really be very much lower than the instantaneous back *E.M.F.* obtained at the moment the polarising current is cut off. The results of Newbery (*loc. cit.*) show clearly the reason for this apparent constancy of the back *E.M.F.* As the speed of the commutator is increased from 250 to 1500 revs. per minute by regular stages of 250 revs., the increase in back *E.M.F.* steadily decreases from about 0·08 volt at the first increase of speed to 0·005 volt at the last; this leads one to imagine that the back *E.M.F.* is gradually reaching a constant value. It should be pointed out, however, that the decrease in the period of contact of the electrode with the potentiometer system is about 0·06 sec. for the first increase of speed, and only 0·004 sec. for the last, and that the corresponding increase of back *E.M.F.* is roughly proportional to these time intervals. The apparent constancy of the back *E.M.F.* is thus due to the fact that there is a large difference in the time intervals involved in a change from 250 to 500 revs. per minute, and a corresponding change from 1250 to 1500 revs. per minute. The apparently constant back *E.M.F.* is thus purely fortuitous, and the results obtained by the ordinary commutator method are of doubtful value.

Previous work (*loc. cit.*) has led to the conclusion that the potential of a polarised electrode measured by the direct method is probably made up of the true potential of the electrode, which is equal to the instantaneous back *E.M.F.*, *plus* an error due to the presence of a resistance at the surface of the electrode. It therefore seemed desirable to investigate the behaviour of the mercury cathode, using the extrapolation method previously applied to the study of the lead electrode, since both the ordinary commutator method and the direct method yield erroneous results. Owing to the fact that the behaviour of a mercury cathode in alkali is considerably affected by the dissolution of deposited alkali metal, only the

cathodic behaviour in acid solution has been investigated in detail. A number of experiments have also been made on the minimum overvoltage, but accurate observation has been difficult; in the first place, the mercury cathode does not give satisfactory results by the graphical method unless the electrolyte is stirred, and, secondly, the commencement of bubble formation is not readily detected. The method adopted in this work was to increase the current very gradually at intervals of 10 minutes, and to observe if any bubbles had formed between the mercury and the glass containing vessel during that interval; when bubbles commenced to form, the potential of the electrode was measured and the minimum overvoltage calculated from it.

Newbery (*loc. cit.*) has described three overvoltage states of mercury, *viz.*, high, low, and zero; the first is said to be permanent at low current densities and is shown by fresh mercury; the second is shown by mercury that has been kept for some time in contact with sulphuric acid and is unstable while current is flowing, whilst the third state is permanent at very high current densities. In the present work, only the highest overvoltage condition has been obtained with any certainty; indications were obtained of the medium condition, but as there appeared to be a gradual transition from this to the higher stage, the lowering of the potential may have been due to the action of mercurous sulphate as a partial depolariser. In any case, this condition was too transient to be investigated in any detail. The zero overvoltage condition has not been observed by the present author, and it has been suggested (Ellingham, *Trans. Faraday Soc.*, 1924, **19**, 825) that this condition may be one of the "depression states" described by Tafel (*loc. cit.*) and attributed by the latter author to the presence of traces of platinum which have been dissolved off from the anode and deposited on the cathode. All the results in the present paper, therefore, deal with the mercury cathode in the condition corresponding to the highest overvoltage state described by Newbery, which may be the only true condition for the measurement of overvoltage.

The results obtained in this work confirm the conclusions drawn from the study of the lead electrode; at very low current values, as long as bubble formation is taking place, the direct potential of a polarised electrode is equal to its instantaneous back *E.M.F.*, but at higher current values the results include an error due to the presence of a resistance at the surface of the electrode. In addition, interesting information has been obtained on the influence of the material of the electrode vessel on the rate of fall of the back *E.M.F.* of the mercury cathode in dilute acid electrolyte after the

polarising current is switched off. As in the case of the lead cathode (this vol., p. 2414), it has been found that the minimum overvoltage is almost independent of the hydrogen-ion concentration of the electrolyte.

## Experimental.

The general experimental method was the same as used in previous work; by means of the commutator, the back *E.M.F.* of the polarised electrode was measured at 0·002, 0·004, 0·006, and 0·012 sec. after the polarising current was switched off, and from these results the potential of the electrode at the moment of breaking the circuit was obtained by extrapolation. The results are compared with those obtained by the direct method.

The mercury used as electrode was a pure commercial product, which was well shaken with dilute nitric acid, and then washed with a rapid stream of water so that the mercury was broken up into small droplets. By treating the mercury in this way before each set of experiments, reproducible results were readily obtained. The electrode vessel varied in different experiments and so the particular type of vessel used is described before each set of results. Connexion with the mercury cathode was made by means of a platinum wire sealed into a glass tube, whilst the anode was a piece of platinum wire, 0·5 cm. long, suspended about 1 cm. above the surface of the cathode. Unless specifically stated, there was no separation of the anode and cathode compartments. The standard electrode used was the $Hg/HgSO_4N\text{-}H_2SO_4$ half-element; the test and standard electrodes were connected in the usual way by means of a tube ending in a jet which was fixed just above the surface of the mercury. All the measured potentials have been roughly corrected for the error due to diffusion potential.

### *Results.*

*Series I.* Electrolyte: 6*N*-sulphuric acid.
Electrode vessel: Glass beaker of 10 sq. cm. cross section.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Temperature: 10°. | | | | | | |
| C.D. (amp./cm.$^2$) ..... | 0·0006 | 0·0012 | 0·0018 | 0·003 | 0·006 | 0·012 | 0·024 |
| Direct Overvoltage ..... | 0·95 | 0·98 | 1·00 | 1·03 | 1·05 | 1·07 | 1·10 |
| Extrapolated „ ..... | 0·95 | 0·96 | 0·97 | 0·98 | 0·99 | 1·00 | 1·01 |
| | Temperature: 70°. | | | | | | |
| Direct Overvoltage ..... | 0·83 | 0·86 | 0·89 | 0·92 | 0·95 | 0·99 | 1·03 |
| Extrapolated „ ..... | 0·83 | 0·83 | 0·84 | 0·85 | 0·86 | 0·87 | 0·88 |

*Series II(a).* Electrolyte: *N*-sulphuric acid.
Electrode vessel: As in Series I.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Temperature: 10°. | | | | | | |
| C.D. ..... | 0·0006 | 0·0012 | 0·0018 | 0·003 | 0·006 | 0·012 | 0·024 |
| Direct Overvoltage ..... | 0·96 | 1·01 | 1·04 | 1·08 | 1·10 | 1·14 | 1·17 |
| Extrapolated „ ..... | 0·95 | 0·96 | 0·97 | 0·98 | 0·98 | 0·99 | 1·00 |
| | Temperature: 70°. | | | | | | |
| Direct Overvoltage ..... | 0·87 | 0·89 | 0·91 | 0·93 | 0·95 | 0·98 | 1·01 |
| Extrapolated „ ..... | 0·81 | 0·82 | 0·83 | 0·84 | 0·85 | 0·86 | 0·87 |

*Series II(b).* Electrolyte: *N*-sulphuric acid.
Electrode vessel: Glass U tube, with limb 1·5 sq. cm. cross section.

| | | | | | | |
|---|---|---|---|---|---|---|
| | Temperature: 10°. | | | | | |
| C.D. ..... | 0·004 | 0·012 | 0·02 | 0·04 | 0·08 | 0·16 |
| Direct Overvoltage ..... | 1·00 | 1·04 | 1·07 | 1·09 | 1·12 | 1·15 |
| Extrapolated „ ..... | 0·97 | 0·98 | 0·99 | 0·99 | 1·00 | 1·01 |

*Series III.* Electrolyte: *N*/16-sulphuric acid.
Electrode vessel: As in Series I, but heated with concentrated acid previous to use.

| | | | | | |
|---|---|---|---|---|---|
| | Temperature: 10°. | | | | |
| C.D. ..... | 0·0018 | 0·003 | 0·006 | 0·012 | 0·024 |
| Direct Overvoltage ..... | 1·07 | 1·11 | 1·15 | 1·20 | 1·25 |
| Extrapolated „ ..... | 0·95 | 0·96 | 0·97 | 0·98 | 0·99 |
| | Temperature: 70°. | | | | |
| Direct Overvoltage ..... | 0·92 | 0·95 | 0·99 | 1·04 | 1·09 |
| Extrapolated „ ..... | 0·83 | 0·84 | 0·85 | 0·86 | 0·87 |

*Series IV.* Electrolyte: *N*/50-sulphuric acid.
Electrode vessel: As in Series III.

| | | | | | |
|---|---|---|---|---|---|
| | Temperature: 10°. | | | | |
| C.D. ..... | 0·0006 | 0·0012 | 0·0018 | 0·003 | 0·006 |
| Direct Overvoltage ..... | 1·00 | 1·08 | 1·12 | 1·17 | 1·24 |
| Extrapolated „ ..... | 0·93 | 0·94 | 0·94 | 0·95 | 0·96 |
| | Temperature: 70°. | | | | |
| Direct Overvoltage ..... | 0·87 | 0·91 | 0·94 | 0·97 | 1·02 |
| Extrapolated „ ..... | 0·80 | 0·81 | 0·81 | 0·82 | 0·83 |

The results given in the above table bear out the statement that at low current densities the overvoltage measured by the direct method is the true overvoltage, provided the electrolyte is not too dilute. With large currents or dilute electrolyte, the error due to surface resistance becomes appreciable; in these circumstances, direct overvoltages are not reliable. It is very probable that at all current densities the instantaneous back *E.M.F.* of the electrode at the moment of switching off the polarising current is equal to the true potential of the electrode while the current is flowing, and hence this value may be used to determine the true overvoltage. A comparison of the results obtained in Series II (*a*) and II (*b*) shows that whereas the direct overvoltage depends on the area of the electrode surface, that obtained by the extrapolation method is independent of this factor.

It has already been found in the case of the lead cathode that the overvoltage is almost independent of the concentration of the sulphuric acid used as electrolyte; from the results quoted above, it appears that the same holds good for the mercury cathode, and an examination of the results obtained by Tafel (*loc. cit.*) at low current densities, when the error due to surface resistance is very small, leads to the same conclusion. The temperature coefficient of overvoltage of the mercury cathode is — 2·1 millivolt per degree, within the range of temperature and dilution of electrolyte in-

vestigated; this figure agrees with that quoted by Bircher and Harkins (*J. Amer. Chem. Soc.*, 1923, **45**, 2897) for 0·1*N*-sulphuric acid.

The variation of the true overvoltage of mercury with current density appears to be small, but the following equation expresses this variation for *N*-sulphuric acid as electrolyte at a temperature of 10°: $E = 0{\cdot}955 + 0{\cdot}028 \log I$, where $I$ is the current density in *milliamps.* per sq. cm. This equation holds, without the introduction of a third constant, even at very low current densities, and hence it appears that very little hydrogen is removed from the mercury cathode by diffusion (see this vol., p. 2414); in confirmation of this it has been found that the "residual current" that can pass without the visible evolution of gas is very small compared with that obtained with a lead cathode of equal area.

*Series V.* It has been found with the lead cathode that the addition of sodium or potassium sulphate to the sulphuric acid electrolyte brought about considerable changes in the cathodic potential, especially at high current densities, even although the hydrogen-ion concentration of the electrolyte was almost unaltered; the same phenomenon has been observed with the mercury cathode, as the results given below indicate.

| Electrolyte. C.D. ..... | 0·0006 | 0·0018 | 0·006 | 0·024 amp./cm.². |
|---|---|---|---|---|
| *N*/16-$H_2SO_4$ ..... | 0·94 | 0·95 | 0·97 | 0·99 volt. |
| *N*/16-$H_2SO_4$ + *N*/16-$K_2SO_4$ ..... | 0·97 | 0·98 | 1·00 | 1·01 |
| *N*/16-$H_2SO_4$ + *N*/4-$K_2SO_4$ ..... | 1·03 | 1·08 | 1·13 | 1·15 |
| *N*/16-$H_2SO_4$ + *N*-$K_2SO_4$ ..... | 1·15 | 1·19 | 1·21 | 1·23 |

There is no doubt that the divergences from the potentials obtained with sulphuric acid alone are due to the fact that there is a simultaneous discharge of hydrogen- and potassium-ions. It is interesting to note that the temperature coefficient of the mercury cathode in the electrolyte containing *N*/16-potassium sulphate in addition to the sulphuric acid is — 0·002 volt per degree at a current density of 0·006 amp./cm.², but when *N*-potassium sulphate is present the temperature coefficient is — 0·0003 volt per degree at the same current density. The first temperature coefficient is the same as in sulphuric acid alone, indicating that in this case hydrogen-ion discharge is the main cathodic process; the second coefficient is almost the same as that of a mercury cathode in potassium hydroxide solution when a potassium amalgam is formed, showing that when the electrolyte contains 1 equiv. of potassium sulphate per litre of *N*/16-sulphuric acid, potassium-ions are being discharged at the cathode. In extending the overvoltage measurements to solutions with small hydrogen-ion concentrations it is clear that the results obtained at appreciable current densities may not be at all comparable with those obtained in sulphuric acid alone, since the

former solutions must of necessity contain other positive ions. The minimum overvoltage, however, has been found to be unaffected by the presence of alkali-metal ions in the electrolyte, since bubble formation at the mercury cathode commences at very low current densities, usually below 0·00002 amp./cm.²

*Minimum Overvoltages.*—It has already been found that at very low current densities the potential of the mercury cathode measured by the direct method may be regarded as the true potential of the electrode; consequently, in measuring the minimum overvoltage the direct method was always used. The method of observation has been outlined above. The following table gives the overvoltages at which gas bubbles first appeared between a mercury cathode and the walls of the glass containing vessel, for electrolytes of different hydrogen-ion concentrations, at a temperature of about 15°.

| Electrolyte. | $p_H$. | Min. Overvoltage. |
|---|---|---|
| *N*-Sulphuric acid ..... | 0 | 0·74 volt. |
| *N*/16 „ ..... | 1 | 0·74 |
| Citrate + $H_2SO_4$ ..... | 4 | 0·75 |
| *N*-Sodium sulphate ..... | 7 | 0·76 |
| *N*-Sodium phosphate ..... | 9 | 0·76 |
| *N*-Sodium hydroxide ..... | 14 | 0·76 |
| *N*-Potassium „ ..... | 14 | 0·76 |

The minimum overvoltage of mercury thus appears to be independent of the hydrogen-ion concentration of the electrolyte; this has been found to be the case, within certain limits, for the lead cathode and is to be expected on theoretical grounds (see previous paper). Even with alkaline electrolytes, in which lead, copper, and iron have lower overvoltages than in acid solutions, the minimum overvoltage of mercury remains constant.

*Further Observations on Series IV.*—During the course of the preliminary investigations with *N*/50-sulphuric acid as electrolyte, when the electrolytic vessel was a glass beaker of 10 sq. cm. cross section which contained mercury to a depth of 0·5 cm., it was found that the electrode potential measured by the direct method increased regularly with increasing current density, but the instantaneous back *E.M.F.* obtained 0·002 sec. after switching off the polarising current, either *decreased* slightly or remained constant as the current density was *increased*. Owing to the high resistance of the electrolyte and the short period of contact of the electrode with the potentiometer system, exact measurement was difficult, but the following figures give a general idea of the behaviour of the electrode.

| C.D. (amp./cm.²) ..... | 0·0006 | 0·0012 | 0·0018 | 0·003 | 0·006 |
|---|---|---|---|---|---|
| Direct Overvoltage ..... | 1·03 | 1·09 | 1·14 | 1·18 | 1·24 |
| Back *E.M.F.* after 0·002 sec. . | 0·91 | 0·91 | 0·89 | 0·87 | 0·87 |

The subsequent rate of fall of the back *E.M.F.* was almost the same in each case, thus leading to the impression that the overvoltage really decreases as the current density is increased; further investigation has proved that this idea was incorrect and that the electrode was behaving abnormally.

During the measurement of the temperature coefficient of this electrode the electrolytic cell was heated in a water-bath while at the same time current was passed through the electrolyte; at first, the electrode behaved as described above, but after some time it became normal, that is, the overvoltage determined by the extrapolation method increased as the current density was increased. On cooling, the electrode still behaved normally, and the overvoltages obtained were similar to those quoted on p. 2650 for *N*/50-sulphuric acid. This curious behaviour was at first attributed to the presence of traces of chloride in the electrolyte, which would be removed as chlorine gas by prolonged electrolysis at elevated temperatures. The original electrolyte, however, was found to contain only infinitesimal traces of chloride and so other causes of the abnormality were sought for.

During the course of further experiments it was found that when the anode and cathode compartments were separated the extrapolated overvoltage was quite normal, that is, it increased regularly as the current density was increased; this was found to be the case either when the mercury was in a glass beaker and the platinum anode in a porous pot, or when the mercury was in the porous pot and the anode in the surrounding electrolyte. If, in the latter case, the platinum anode was placed inside the porous pot too, then the electrode still behaved in a fairly normal manner, but on pouring the same mercury and electrolyte into a clean glass beaker the overvoltage as measured by the back *E.M.F.* was again abnormal if the anode and cathode compartments were not separated. This suggested that the abnormal behaviour was connected with the diffusion of oxygen * from the anode, and also with the material of the vessel that contained the mercury; further experiments confirmed this view. When the bottom of the glass vessel hitherto in use was coated internally with either paraffin wax or stearic acid, the electrode behaved normally even if the anode and cathode compartments were not separated; if the protective layer was scraped off, then the same electrode and electrolyte gave abnormal results unless the compartments were separated.

* This point has been verified as follows. The mercury was placed in a glass beaker, and the anode in a porous pot: the electrode behaved normally. If air or oxygen was bubbled gently through the electrolyte, the results were the same as if the anode and cathode were not separated.

By allowing the glass beaker to stand or be heated with concentrated sulphuric acid and then rinsing out with dilute acid, the electrode behaved normally; if the same vessel was heated with alkali, then the electrode was abnormal.

*Discussion.*

Dunnill (*loc. cit.*) has stated that the surface of a mercury cathode in sulphuric acid moves rapidly away from the centre immediately after receiving current, and during the course of the present work it has been observed that there is a force acting either on the mercury surface or on the thin layer of electrolyte in contact with this surface, pulling it towards the circumference of the containing vessel. The presence of this force may be noted if the polarising current is suddenly switched off, when there is seen to be a rush of bubbles from the circumference to the centre of the mercury surface; the intensity of the force appears to increase as the current increases. At high current densities, when the mercury surface is in a state of high tension, there is probably a comparatively large concentration of electromotively active material, which is the cause of the high overvoltage, at the thin layer of electrolyte which separates the electrode vessel and the circumference of the mercury cathode. In certain circumstances, the material of the vessel appears to exert a catalytic influence on the reaction between the electromotively active material and oxygen that has diffused from the anode, so that combination is accelerated. When the polarising current is cut off there is thus a rapid fall of potential, which could not be measured with the apparatus used in this work, followed by a much slower decrease in back *E.M.F.* corresponding with that which occurs normally when the mercury surface is relaxed. By coating the active glass surface with paraffin wax or stearic acid, or by digesting it with concentrated acid, it is made to lose its catalytic activity, although the surface tension forces still appear to be operative; a porous earthenware vessel even without previous treatment has very little catalytic effect. If a glass vessel, on the other hand, is heated with alkali, its catalytic activity appears to be increased. By separating the anode and cathode compartments, the anodic oxygen cannot reach the cathode and consequently the fall of back *E.M.F.* after the polarising current is switched off is always normal no matter what is the material of the electrode vessel. At low current densities the surface tension forces are much smaller and comparatively little of the electromotively active material is present at the circumference of the mercury; hence the initial fall of potential is extremely small, and the only fall observed is that due to the normal removal

of the active material. It is thus possible to explain the fact that in some circumstances the back *E.M.F.* obtained 0·002 sec. after switching off a large polarising current may be smaller than that measured under similar conditions with a smaller current.

Strictly speaking, the catalytic effect of the electrode vessel should also influence the potential measured by the direct method. Unfortunately, in the present work, the catalytic effect was only observed with very dilute acid electrolytes, when the errors due to surface resistance were large and uncertain, and these would mask any slight alterations in the true potential of the electrode. It is possible, however, that if the electrode vessel were made of a strongly alkaline glass the catalytic effect might become noticeable with more concentrated acid electrolytes. How far this may account for the steady decrease in the cathodic overvoltage of mercury in *N*-sulphuric acid measured by Newbery (*loc. cit.*), using the older commutator method, as the current density is increased, is open to conjecture.

Since the catalytic activity of the electrode vessel appears to be enhanced by treatment with alkali, it is clear that the abnormality in the back *E.M.F.* should be most noticeable when an alkaline electrolyte is being used; unfortunately, in these circumstances, particularly at high current densities, the mercury dissolves a considerable amount of the deposited alkali metal and the potential remains constant for some time after the polarising current is switched off.

*Summary.*

(1) It has been shown that at low current densities, and with not too dilute electrolyte, the potential of the mercury cathode in sulphuric acid measured by the direct method is almost equal to the instantaneous back *E.M.F.*, and so the true overvoltage may be calculated from the former.

(2) At high current densities, the direct and extrapolated overvoltages have been found to differ; this difference increases as the concentration of the electrolyte is decreased, but decreases with increasing temperature. It is thus probably due to the presence of a resistance at the surface of the electrode.

(3) The cathodic overvoltage of mercury in sulphuric acid, at appreciable current densities, does not vary very greatly as the concentration of the electrolyte is changed from $N/50$ to $6N$.

(4) The minimum overvoltage appears to be a constant independent of the hydrogen-ion concentration of the electrolyte, even in alkaline solutions.

(5) With dilute electrolytes it has been found that oxygen

diffusing from the anode may influence the rate of fall of the back *E.M.F.* of the mercury cathode in a manner which depends on the material of the electrode vessel and the current density.

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## CCCLXIII.—*The Atomic Weights of Carbon and Silver.*

By GEORGE DEAN.

THE work described below arose out of a previous attempt to determine the atomic weight of nitrogen combined in the cyanogen radical (J., 1900, **77**, 117). A known weight of silver cyanide was dissolved in nitric or sulphuric acid, and the amount of silver present found by titration with potassium bromide. The weight of cyanogen combined with one gram-atom of silver was thus obtained; deducting the atomic weight of carbon, that of nitrogen remains.

The value so obtained depends on the assumption that the atomic weights of silver and carbon are known. At that time these were supposed to be established, whereas there was a distinct discrepancy between the older value for nitrogen, based on chemical methods, and that obtained by physical means. The position is now reversed. The value for nitrogen is known with great exactness, whilst that for carbon has been called in question (Scott, J., 1897, **71**, 550; Moles, *J. Chim. Phys.*, 1917, **15**, 51). In the circumstances, it was thought that the value for the equivalent of cyanogen could be used to better purpose in determining the atomic weight of carbon.

In the experiments described below, the previous method was simplified. Silver cyanide was reduced in hydrogen and the silver weighed direct. By thus avoiding the use of potassium bromide the risk of loss in transferring solutions for titration was eliminated.

A second and independent value for the atomic weight of carbon was obtained by converting weighed quantities of silver cyanate directly into the metal.

Finally, by combining the results of the two series of experiments, and proceeding from the standard value O = 16, new values were deduced for the atomic weight of silver and the equivalent of cyanogen on that basis alone.

### *Determination of the Atomic Weight of Carbon by Reduction of Silver Cyanide to Silver.*

*Preparation of Silver Cyanide.*—Silver sulphate was precipitated from a solution of recrystallised silver nitrate by adding a slight

excess of dilute, redistilled sulphuric acid. The finely crystalline powder was well washed to remove the acids and recrystallised from a large volume of water.

Hydrocyanic acid solution was prepared by distilling together potassium ferrocyanide and dilute sulphuric acid. The solution was always redistilled before use, and the middle fraction only retained. The finely divided ferrocyanide was obtained from Kahlbaum's purest product by recrystallising twice.

Dilute solutions of the silver sulphate and hydrocyanic acid (in slight excess) were shaken in a large stoppered bottle, the slightly turbid liquid was decanted from the precipitated cyanide and replaced by more of the solutions. When a sufficient quantity had been obtained, the silver cyanide was washed with water until the washings were free from sulphuric acid, and thereafter for some months. During this time it was kept in the dark (although apparently little sensitive to the action of light). The lengthened period of washing should enable traces of acid—possibly enclosed in the flocculi—to diffuse out. The liquid was poured off and the pure white mass dried in a vacuum over sodium hydroxide. Before opening the desiccator, either to renew the sodium hydroxide, or to transfer the cyanide, purified, dried air was slowly admitted.

*Method.*—Two small flasks were chosen of as nearly as possible the same volume (about 150 c.c.) and weight—one to hold the silver cyanide, the other to serve as its counterpoise. A glass headpiece, carrying inlet and outlet tubes, was ground to fit the former. The headpiece was not weighed with the flask. The counterpoise flask was made almost equal in weight to the reaction flask by adding a few scraps of the same glass. Both were then thoroughly cleansed with boiling nitric acid and water, dried by heating in a flame, polished with a fine linen cloth, brushed with a camel-hair brush to remove a minute fibre or two, again passed through the flame, and set aside on the clean copper plate of a large desiccator to cool. They were then placed on the balance pans, and the rider moved to the milligram mark nearest the position for exact equipoise. The final weighing was made in the early morning of the following day, when the temperature of the room was steady. The method of swings was used, as described later under "Weighing."

The details of an experiment are given: $w$ = weight of the counterpoise.

The flask after the treatment described weighed $w + 0{\cdot}00099$ g., and $w + 0{\cdot}00101$ g. after being again polished, heated, etc.

Silver cyanide which had been drying for months in a silica dish

in a vacuum was then added to the reaction flask by means of a long-stemmed glass funnel.

The weight of the flask and silver cyanide was $w + 11{\cdot}57679$ g.

[In transferring the cyanide, a silver spatula was used. Through the friction occasioned, the substance became highly electrified, and particles clung firmly to the sides of the flask. On gently tapping it, after it had stood in the balance case for a few hours, these separated particles readily joined the main portion. It was assumed that any charge, either on the cyanide or the flask, was dissipated during the interval (over-night) the flask was kept on the pans of the balance before weighing. That this was so is indicated by the close agreement of a second weighing, made an hour or so later, with the first, whereas there was a distinct, though small, variation in the weighings taken immediately after transferring the cyanide to the flask.]

To make sure of the expulsion of the last traces of moisture from the cyanide, the flask was fitted with the headpiece, placed in a V. Meyer crucible oven containing water, and air, thoroughly washed by sodium hydroxide solution, dried by passing through several feet of the ground solid, and filtered through glass wool, was slowly driven through the apparatus at 100°. After it had been heated for several days, the flask was removed while still warm, polished, etc., and weighed. The weights of the flask and cyanide, after 38 and 41 hours' heating at 100°, were $w + 11{\cdot}57663$ and $w + 11{\cdot}57679$ g., respectively. The water in the oven jacket was next replaced by xylene (b. p. 132°), and the heating continued at the higher temperature until, after 128 hours, the constant weight $w + 11{\cdot}57651$ g. was attained (11·57650—11·57653).

The flask was now placed in an air-oven, and a slow current of dry nitrogen passed through; this was in turn displaced by dry hydrogen (prepared by the electrolysis of barium hydroxide solution). The temperature was gradually raised until hydrogen cyanide (detected by silver nitrate in a wash-bottle) was freely evolved. The first signs were noticed at about 220°, and ceased after about 3 hours' heating, the temperature having been gradually raised to 270°. A few drops of clear liquid * condensed in the cool part of the outlet tube as the reduction proceeded. It slowly crystallised, changed to tar, and finally charred. When the gas no longer affected the silver nitrate, the flask was removed and a slight

* The possibility that this liquid might have been a volatile silver compound would seem to be precluded by the fact that the outlet tube, after being heated to redness to burn off the charred film, was perfectly bright; it would have become discoloured, had silver been present.

brown film, possibly paracyanogen, which had deposited in the neck, was burnt away. The silver at this stage was grey and bulky. The heating was continued at a higher temperature (about 300°) alternately in hydrogen, and air or oxygen, until a constant weight was reached. This took some weeks, the last traces of volatile matter only being removed with difficulty. The silver was finally obtained as a shrunk mass, perfectly white. The results obtained in the successive weighings are given below.

| Hours of heating. | Current of gas. | Wt. in g. of flask and silver = $w$ + | Hours of heating. | Current of gas. | Wt. in g. of flask and silver = $w$ + |
|---|---|---|---|---|---|
| 52 | Hydrogen | 9·33477 | 7 | Hydrogen | 9·32974 |
| 12 | Nitrogen | | 9 | Oxygen | 9·33008 |
| 59 | Air | 9·33040 | 10 | Hydrogen | 9·32972 |
| 32 | Hydrogen | 9·33034 | 2½ | Hydrogen | 9·32972 |
| 56 | Air | 9·33025 | 5 | Nitrogen | |
| 55 | Air, hydrogen, nitrogen, and finally oxygen | 9·33026 | 58 | Air | 9·32988 |
| | | | 8½ | Hydrogen | 9·32973 |
| 32 | Air | 9·32990 | | | |
| 11 | Hydrogen | | | | |

*Corrections.*—In working out the results from the experimental figures, two points have to be considered: (1) the selection of the right weighings, both of cyanide and silver, from the many taken, (2) the application of corrections for the errors in the set of weights used, and the buoyancy of the materials.

In the case of the experiment given above, the following were selected:

Weight of empty flask (mean of two) = $w$ + 0·00100.
Weight of flask + AgCN (mean of last four) = $w$ + 11·57651.
Weight of flask + Ag (mean of last four in hydrogen) = $w$ + 9·32973.
Corrected wt. of AgCN = 11·57551 + 0·00104 (wt. corr.) + 0·00178 (buoyancy corr.) = 11·57833.
Corrected wt. of Ag = 9·32873 + 0·00058 (wt. corr.) − 0·00028 (buoyancy corr.) = 9·32903.

In this experiment, then, it has been found that 11·57833 g. of AgCN contain 9·32903 g. of Ag. The "equivalent weight" of AgCN, containing 107·88 of silver, from these data will be 133·8910. Deducting Ag 107·88 + N 14·008,

C = 12·003.

(The densities used were AgCN 4·06, Ag 10·45, brass 8·4, Pt 21·5, air 0·00122.)

*Results.*

*Series A.*

| Expt. | Sample. | Wt. of AgCN (g.). | Wt. of Ag (g.). | Equivalent of AgCN. | Atomic weight of carbon. |
|---|---|---|---|---|---|
| I. | A | 8·09287 | 6·52019 | 133·9009 | 12·0129 |
| II. | B | 11·27484 | 9·08419 | 133·8952 | 12·0072 |
| III. | B | 16·31000 | 13·14112 | 133·8944 | 12·0064 |
| IV. | B | 13·58968 | 10·94942 | 133·8934 | 12·0054 |
| V. | B | 13·63559 | 10·98669 | 133·8896 | 12·0016 |
| VI. | C | 13·00330 | 10·47853 | 133·8733 | 11·9853 |
| VII. | C | 11·25209 | 9·06669 | 133·8829 | 11·9949 |
| VIII. | C | 19·59057 | 15·78523 | 133·8865 | 11·9985 |
| IX. | B | 10·74440 | 8·65677 | 133·8957 | 12·0077 |
| X. | C | 10·48999 | 8·45191 | 133·8941 | 12·0061 |

The mean value for the atomic weight of carbon from the ten determinations is :

$$12{\cdot}0026 \pm 0{\cdot}0017.$$

Separate batches of silver cyanide were made from time to time, and are indicated by the letters in the second column. In Expt. I, the reduction was carried out in a different piece of apparatus. The cyanide was contained in a porcelain crucible enclosed in a glass case, perforated for the admission of hydrogen. It was the only one of several attempts which was completed without mishap, and is included in this series.

Several of the hard glass flasks used failed to stand the long-continued heating. Either the head-piece itself cracked, or the ground neck at the place where it fitted. Accordingly, a second series of experiments was carried out in apparatus of transparent silica ware. This had the further advantage that any film of carbonaceous matter deposited in the neck during the reduction could be burnt off without risk of fracture. The flasks, made for these experiments by the Silica Syndicate, Ltd., were in pairs, the reaction flask and counterpoise, as in the previous experiments, being of approximately the same weight and volume, and therefore extent of surface.

*Series B.*

| Expt. | Sample. | Wt. of AgCN (g.). | Wt. of Ag (g.). | Equivalent AgCN. | Atomic weight of carbon. |
|---|---|---|---|---|---|
| XI. | C | 12·78888 | 10·30454 | 133·8882 | 12·0002 |
| XII. | D | 12·34522 | 9·94716 | 133·8876 | 11·9996 |
| XIII. | D | 13·55745 | 10·92354 | 133·8923 | 12·0043 |
| XIV. | D | 11·57833 | 9·32901 | 133·8910 | 12·0030 |
| XV. | D | 13·22384 | 10·65417 | 133·8995 | 12·0115 |
| XVI. | C | 11·02014 | 8·87968 | 133·8847 | 11·9967 |

The mean value from the six determinations is :

$$12{\cdot}0026 \pm 0{\cdot}0014.$$

The silver cyanide D differed from the other specimens used. The sulphate from which it was made had been subjected to further

recrystallisation, and the hydrocyanic acid solution to a second redistillation.

In a third series of experiments an attempt was made to separate a specimen of silver cyanide into fractions, and to compare the values for the atomic weight determined from each. The cyanide, prepared in the same way as D, was suspended in water, and ammonia passed in. The hot liquor was poured off from the still undissolved cyanide, replaced by more water, and the ammonia again passed in. This was repeated until most of the substance had dissolved. Three sets of extracts were thus obtained—the first, middle, and final. On cooling, each of these deposited the fine, scaly crystals of the ammonia compound, $AgCN,NH_3$. On heating, these redissolved. Each solution was then treated with dilute sulphuric acid in excess, the precipitated silver cyanide left with more acid, and finally washed over a period of some months to remove every trace of sulphate. In this way, about 50 g. of cyanide were obtained in three fractions—E the first, F the middle, and G the final.

*Series C.*

| Expt. | Sample. | Wt. of AgCN (g.). | Wt. of Ag (g.). | Equivalent AgCN. | Atomic weight of carbon. |
|---|---|---|---|---|---|
| XVII. | F | 10·65300 | 8·58302 | 133·8976 | 12·0096 |
| XVIII. | F | 12·87330 | 10·37157 | 133·9017 | 12·0137 |
| XIX. | E | 7·18106 | 5·78649 | 133·8797 | 11·9917 |
| XX. | G | 8·45664 | 6·81430 | 133·8805 | 11·9925 |
| XXI. | G | 10·82781 | 8·72440 | 133·8893 | 12·0013 |

The mean value for carbon in Series *C* is:

$$12{\cdot}0018 \pm 0{\cdot}0047.$$

*Discussion of Results.*

Attributing equal weight to each of the twenty-one experiments,

$$C = 12{\cdot}0024 \pm 0{\cdot}0011.$$

This value is almost identical with that obtained in Series *A* and *B* ($C = 12{\cdot}0026$). Of the three sets of experiments, I would give the preference to *B*. The use of silica flasks gives it the advantage over Series *A*, whilst the cyanide used, made from very dilute solutions of silver sulphate and hydrocyanic acid, was probably superior to that obtained by reprecipitating it with acid from solution in ammonia, and used in Series *C*. In the latter case there is the possibility of traces of the ammonia compound remaining undecomposed by the acid.

*Determination of the Atomic Weight of Carbon by Reduction of Silver Cyanate to Silver.*

A second and quite independent value for the atomic weight of carbon was obtained by using silver cyanate instead of the cyanide.

By reducing a known weight of cyanate to silver, the weight of the radical (CNO) combined with the atomic weight of silver—107·88—can be determined. This value is the sum of the atomic weights of carbon, nitrogen, and oxygen. Deducting those for nitrogen and oxygen, that for carbon remains.

The atomic weight for carbon so obtained is thus based on the three values O = 16, Ag = 107·88, N = 14·008.

A chance observation provided the method. A weighed amount of the cyanate had been taken for treatment with bromine. To make sure that it was quite free from moisture, it was left in an air-oven at about 105° for some time. The temperature rose somewhat, and on opening the oven it was found that the cyanate had darkened, and lost weight. After some hours it had turned white again, and the weight showed that it had been reduced to silver.

The change was attributed to the action of the moisture in the heated air, metallic cyanates being readily converted into carbonates:

$$2AgCNO + 3H_2O = Ag_2CO_3 + 2NH_3 + CO_2.$$
$$2Ag_2CO_3 = 4Ag + 2CO_2 + O_2.$$

(When the change was effected in a flask, a few small isolated glassy crystals, apparently of carbamide, were deposited in the continuation of the outlet tube. They dissolved in a drop of water, and responded to the nitrate and biuret tests.)

*Preparation of Silver Cyanate.*—This was obtained by heating together carbamide and silver nitrate in solution:

$$AgNO_3 + CO(NH_2)_2 = AgCNO + NH_4NO_3.$$

Kahlbaum's purest carbamide was dissolved in water, and a little silver nitrate solution added. A faint pink coloration developed which gradually darkened and, after a day or two, a trace of reduced silver separated. The clear liquor was decanted, and heated with a solution of pure recrystallised silver nitrate (added in distinct excess) on a water-bath until fine, hair-like crystals began to separate. When a small deposit of these had formed, the liquor was poured off, and heated until there was no perceptible increase in the amount of cyanate separated. The hot liquor was poured off and the precipitate quickly washed with repeated changes of boiling water. (If allowed to remain with the crystals, the liquor usually deposits a slight coating of silver carbonate.) The washed crystals were suspended in water and ammonia was passed in until most of them had dissolved. As solution proceeded, the temperature rose and the undissolved crystals formed a caked mass—probably $AgCNO,NH_3$. This slowly diminished in quantity and when but little remained the hot liquor was poured off and allowed to stand; large crystals of the ammonia compound then formed. The clear

liquor was removed, and treated with dilute, redistilled sulphuric acid, which had been treated with a solution of pure silver sulphate. This was added until the pure white cyanate was all thrown out, and the excess of acid reacted with it sufficiently to produce a considerable effervescence of carbon dioxide. The hot liquor was poured off, and the precipitate thoroughly washed with hot water until it was free from sulphates. As with the cyanide, the washing was continued in the dark for an extended period. The precipitate was finally drained and transferred to a vacuum desiccator containing coarsely ground sodium hydroxide. The hydroxide was frequently renewed during the first stage of the drying.

*Method.*—In carrying out a determination, two porcelain crucibles with lids were selected, of the same reputed volume, and as nearly as possible of the same weight; approximate equality being attained by slightly grinding down the edge of the lid of the heavier. This crucible served as counterpoise to the other. Both were thoroughly cleansed and ignited, and the slight difference in weight was carefully ascertained. Silver cyanate was then placed in the one, weighed, and left drying in a vacuum until the weight was constant. There was usually little variation during several months.

The crucible with the cyanate was next enclosed in a small glass case, which had been perforated for the admission of a current of air or hydrogen, and heated in a Victor Meyer crucible oven. At first, purified, moist air was passed through the apparatus at the temperature of boiling aniline (180°). Towards the end the temperature was raised by using other liquids of suitable boiling point in the oven, *e.g.* diethylaniline (213°) and diphenylamine (310°). As in the case of silver cyanide, the removal of the last traces of volatile matter required long-continued heating, alternately in air and hydrogen.

The results obtained in the first series of experiments are as follows:

*Series A.*

| Expt. | Wt. of AgCNO (g.). | Wt. of Ag (g.). | Equivalent of AgCNO. | Atomic weight of carbon. |
|---|---|---|---|---|
| I. | 9·06436 | 6·52393 | 149·8889 | 12·0009 |
| II. | 6·32084 | 4·54946 | 149·8843 | 11·9963 |
| III. | 8·62108 | 6·20492 | 149·8878 | 11·9998 |
| IV. | 6·86108 | 4·93828 | 149·8848 | 11·9968 |
| V. | 14·74115 | 10·61003 | 149·8842 | 11·9962 |
| VI. | 10·58756 | 7·61992 | 149·8947 | 12·0067 |
| VII. | 9·85865 | 7·09569 | 149·8871 | 11·9991 |
| VIII. | 10·80524 | 7·77683 | 149·8900 | 12·0020 |

Mean, C = 11·9997 ± 0·0008.

In the next series, the means taken to obtain pure material were more elaborate. The silver nitrate was heated for some

time with nitric acid (the diluted middle fraction obtained on distillation of commercial "pure" acid). On cooling quickly, fine crystals were obtained. These were well drained, washed, and recrystallised from water. Concentrated solutions of the nitrate thus obtained and carbamide were mixed and cooled, and the compound $AgNO_3,CO(NH)_2$ was separated, drained, washed, dissolved in water, and the solution heated to give silver cyanate. The separated cyanate was well washed, suspended in water, and ammonia passed in. Solution was effected in three stages. Each fraction was precipitated by adding dilute sulphuric acid, the first portion of the precipitate being rejected in each case.

An attempt was made to collect only the middle portion by pouring off the liquor while still alkaline with free ammonia. The cyanate thus prepared was then subjected to a thorough washing, first with water containing a few drops of (sulphuric) acid, and finally with water alone.

*Series B.*

| Expt. | Wt. of AgCNO (g.). | Wt. of of Ag (g.). | Equivalent of AgCNO. | Atomic weight of carbon. |
|---|---|---|---|---|
| IX. | 10·95568 | 7·88354 | 149·9198 | 12·0318 |
| X. | 15·41320 | 11·09163 | 149·9126 | 12·0246 |
| XI. | 15·88829 | 11·43487 | 149·8949 | 12·0069 |
| XII. | 7·36851 | 5·30337 | 149·8886 | 12·0006 |
| XIII. | 7·44756 | 5·36002 | 149·8955 | 12·0075 |
| XIV. | 12·52765 | 9·01405 | 149·9307 | 12·0427 |
| XV. | 13·47481 | 9·69587 | 149·9260 | 12·0380 |
| XVI. | 18·29697 | 13·16456 | 149·9387 | 12·0507 |
| XVII. | 18·22897 | 13·11874 | 149·9032 | 12·0152 |

Mean, C = 12·0242±0·0039.

In Expts. IX to XIII, the cyanate was contained in crucibles as described above. In Expts. XIV to XVII, it was enclosed in stoppered flasks, as in the cyanide experiments. The latter arrangement prolonged the time required for complete decomposition of the cyanate, but prevented any chance of traces of impurities entering from the outside air.

After the pains taken to refine the cyanate still further, the results of this series of experiments were disappointing. They vary among themselves much more than those in Series *A*, and give a distinctly higher mean value for the equivalent of silver cyanate—149·9122 against 149·8877.

The high value for the equivalent found in most of the experiments can be attributed to the presence of the compound $AgCNO,NH_3$ in the cyanate. This can be explained as follows. In attempting to precipitate the cyanate in fractions from its solution in ammonia, the soluble $AgCNO,NH_3$ is decomposed by the sulphuric acid, which removes the ammonia. Consequently,

the sparingly soluble silver cyanate is precipitated progressively as the acid is added. So long as the solution is alkaline the ammonia compound is present. (If the solution is cooled, the compound appears in minute, glistening scales.) As the middle fractions of cyanate used were deposited while the solution was still alkaline, there was the possibility of the ammonia compound being precipitated also. To minimise this, the hot liquor was immediately poured off, and the precipitate flooded with boiling water containing a little sulphuric acid. This treatment was repeated several times. The washing was continued with acidified water for some weeks and completed with pure water. In spite of these precautions there was apparently still undecomposed ammonia compound present.

To eliminate, if possible, any error due to this cause in the final experiments, the material was prepared in a slightly different way. The fractionation was carried out as before, with the mother-liquor still alkaline, but the cyanate was finally precipitated in presence of excess of acid. To ensure this, the cyanate, thrice refined by fractional precipitation, was dissolved by means of ammonia, and a portion of the solution titrated with the sulphuric acid. A measured excess of acid was then added to the remainder of the ammoniacal solution, *sufficient not only to neutralise the ammonia, but also to decompose a good proportion of the cyanate itself.* There was a vigorous evolution of gas due to the latter reaction.

This procedure should favour the precipitation of cyanate free from the ammonia compound.

A portion, X, was removed after washing for some months, and dried in a vacuum; the remainder, Y, was washed for a longer period. Z was prepared from the considerable quantity of rejected fractions, by a repetition of the treatment described.

*Series C.*

| Expt. | Wt. of AgCNO (g.). | Wt. of Ag (g.). | Equivalent of AgCNO. | Atomic weight of carbon. | Sample. |
|---|---|---|---|---|---|
| XVIII. | 11·75141 | 8·45731 | 149·8989 | 12·0109 | Z |
| XIX. | 11·93035 | 8·58648 | 149·8922 | 12·0042 | X |
| XX. | 10·73580 | 7·72683 | 149·8906 | 12·0026 | Y |
| XXI. | 5·01536 | 3·60973 | 149·8884 | 12·0004 | Y |

Mean, C = 12·0045±0·0020.

*Discussion of Results.*

The conclusions arrived at from the three series of experiments may be briefly stated as follows:

*Series* A.—The different specimens of cyanate used were reprecipitated from ammonia—usually more than once—but always by using *excess* of acid. There was thus decomposition of part of the

cyanate so precipitated, by the further action of the acid—so much so that in some cases considerable quantities of silver sulphate crystals had to be removed in the washing.

The final values are consistent.

*Series B.*—Further refining of the cyanate was attempted by fractional precipitation from solution in ammonia, by addition of a quantity of sulphuric acid insufficient fully to neutralise the ammonia. The final values fall into two groups. In one, they are in close agreement with those of Series *A*—in the other they are much higher. (Mean values for equivalent of AgCNO: Series *A*, 149·8877; Series *B*, 149·8955 and 149·9256.)

The higher values can be explained by the presence of an ammonia compound. This is readily obtained and has been observed on cooling the hot, partly neutralised solutions. If this is the correct explanation, cyanate precipitated from acid solutions might be expected to yield values in agreement with those of Series *A*.

*Series C.*—A specimen was fractionated, dissolved in ammonia, and finally precipitated from hot solution by adding excess of acid. The values deduced in this series (mean 149·8925) are substantially the same as in Series *A* (149·8877).

On these grounds, Expts. IX, X, XIV, XV, and XVI have been rejected in arriving at the mean. (Expts. XIV, XV, and XVI were carried out with portions of the same specimen which differed only in the extent of the washing).

The mean value for the equivalent weight of silver cyanate from the sixteen experiments accepted is 149·8909, and for the atomic weight of carbon, 12·0029 $\pm$ 0·0009.

### *The Atomic Weight of Silver, and the Equivalent Weight of Cyanogen, by Direct Reference to Oxygen.*

The value for the atomic weight of carbon obtained from the silver cyanate experiments thus agrees closely with that derived from the cyanide.

The object in carrying out the cyanate experiments, however, was not the confirmation of the cyanide result. It was more fundamental. The values for the atomic weight of carbon deduced from the two sets of experiments, and given above, depend on the accepted atomic weights of silver (107·88), nitrogen (14·008), and oxygen (16). By combining the results of the cyanide and cyanate experiments it is possible, however, to deduce a new and independent value for the atomic weight of silver, and at the same time for the equivalent weight of cyanogen. This involves the assumption of no other atomic weight than the basic O = 16.

The steps by which the new values were derived from the experimental numbers are briefly as follows:

Let (AgCN) represent the equivalent weight of silver cyanide, each of the symbols standing for the atomic weight of the element when O = 16. Similarly, the equivalent weight of silver cyanate will be represented by (AgCN) + 16.

The two equivalents are in a definite fixed ratio—call it $X/Y$. This ratio is the same as that between any two weights of silver cyanate and cyanide, which contain the same weight of silver. Take for our purpose the weights of cyanate and cyanide which contain 100 parts of silver. In the actual experiments,

165·22621 g. of silver cyanate gave 118·91641 g. of silver;
252·48900 „ „ cyanide „ 203·43862 „ „

From these results the weights which contain 100 g. of silver are respectively 138·94317 g. and 124·11064 g. Then

$$\frac{(AgCN) + 16}{(AgCN)} = \frac{X}{Y} = \frac{138{\cdot}94317}{124{\cdot}11064}.$$

From this, (AgCN) = 133·879.

The weight of silver in this amount of cyanide is the atomic weight. It is readily calculated from the experimental numbers for silver cyanide given above:

$$Ag = 133{\cdot}879 \times 100/124{\cdot}11064 = 107{\cdot}871.$$

And (CN) = 26·008.

There are two distinct advantages in combining the results of the cyanide and cyanate experiments for the purpose of deducing the atomic weight of silver and the equivalent of cyanogen:

1. In each case the silver salt is reduced in the one vessel, and the silver weighed. There is thus no transference, and no indirect estimation.

2. In both the treatment is very similar; the experimental errors are of the same nature and approximately the same magnitude; in the final result they should largely neutralise one another.

*Summary of Results.*

1. From the ratio AgCN : Ag, assuming O = 16, Ag = 107·88, N = 14·008,
$$C = 12{\cdot}002 \pm 0{\cdot}001.$$
2. Similarly, from the ratio AgCNO : Ag,
$$C = 12{\cdot}003 \pm 0{\cdot}001.$$
3. By combining the two ratios and assuming only that O = 16,
$$Ag = 107{\cdot}871.$$
$$(CN) = 26{\cdot}008.$$
4. From 3, and assuming that N = 14·008,
$$C = 12{\cdot}000.$$

*Notes on Work Arising from the Above.*

*Weighing.*—The method of swings was used. The flask with its contents was placed on the left pan, the counterpoise and weights on the right. After adjusting with rider to the nearest milligram, they were left in the balance all night. Next morning, the equilibrium point of the needle was obtained from the extent of the swings. The rider was then moved along the beam to the next milligram mark, and readings were again taken. From the two equilibrium positions the displacement corresponding to the addition of one mg. to the weight was calculated. Finally, the flasks and weights were removed, the balance was left for a time to come to a steady temperature, and again allowed to swing to get its true point of equilibrium on the scale. From the three positions the weight is readily obtained.

Experiments were made with the balance to test whether it could be relied on to give consistent weighings over the period usually required to complete a determination. A silica flask, reserved for the purpose, was weighed at intervals against its counterpoise. The variations in the recorded weight were negligible (J., 1919, **115**, 406).

*A Final Correction.*—The weights (by Sartorius) were calibrated in the usual way by weighing each piece alternately in the left and right pan against other pieces of the set, of equal nominal weight. They were then expressed in terms of a unit, which was 1/200th part of the total nominal weight of the (platinised) brass pieces—200 g. This process was repeated twice during the course of the work, and the slight alterations in the values of the pieces were allowed for in succeeding experiments.

The smaller pieces are of platinum, and in the first correction of the weights of silver, cyanide, and cyanate for the air displaced, the density of platinum was used to obtain their volumes. Gray and Burt (J., 1909, **95**, 1636) have pointed out that this is superfluous when the set has been calibrated in terms of the brass weights. In the final weights given above, this over-correction has been rectified. In the majority of the experiments the platinum weights bore only a small proportion to the brass. The correction, however, would have had an appreciable effect, but for the fact that it was negative in sign both for the cyanide and cyanate, on the one hand, and the silver on the other, and so was largely eliminated in the results.

*Densities.*—As the cyanide, cyanate, and silver weighed in the experiments were probably in slightly different physical forms from those whose densities are given in the published tables, their values were found independently for use in correcting the weights for displacement of air.

(a) *Silver cyanide.*—By direct comparison with water the following results were obtained: 1 c.c. weighed 4·058 g. at 5°, 4·057 g. at 10°, 4·057 g. at 15°, and 4·052 g. at 20°.

(b) *Silver cyanate.*—As this is appreciably soluble in water, it was weighed in benzene, which was then compared with water: 1 c.c. at 19° weighed 4·164 g.

(c) *Silver.*—At the moderate temperatures employed in the reductions, this was obtained as a matted, semi-coherent mass: 1 c.c. weighed 10·487 g. at 10°, 10·462 g. at 15°, and 10·440 g. at 20°.

### *Action of Silver on Silica Flasks.*

Even at the moderately low temperatures employed in the final reduction, there was a perceptible effect where the silver had rested on the flask. In the case of "resistance" glass there was a pronounced brown colour after one reduction. The pure silica ware was only slightly discoloured after several. This action is accompanied by a gradual increase in weight, as the following numbers show.

A new silica flask and its counterpoise were treated with boiling nitric acid, ignited, cooled, and weighed. Several reductions were carried out in the flask. After each the silver was removed, and the flask alone treated with boiling acid and weighed against the unchanged counterpoise, ready for the next experiment. The weight given below is that required to bring the counterpoise into equilibrium with the flask. In each case it is the mean of several concordant weighings.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Wt. of new flask | = | Counter. | − 0·46 | mg. | | | | |
| „ after Expt. 1 | = | „ | − 0·35 | „ | Increase | 0·11 | mg. |
| „ „ „ 2 | = | „ | − 0·19 | „ | „ | 0·16 | „ |
| „ „ „ 3 | = | „ | − 0·08 | „ | „ | 0·11 | „ |
| „ „ 4 | = | „ | − 0·05 | „ | „ | 0·03 | „ |
| „ „ „ 5 | = | „ | + 0·11 | „ | „ | 0·16 | „ |
| „ „ „ 6 | = | „ | + 0·34 | „ | „ | 0·23 | „ |

The total increase during six experiments was thus 0·80 mg., or, on an average, 0·13 mg. per experiment. If it is due to the formation of silver silicate while silver is heated in contact with silica in an oxidising atmosphere, the weight of silver finally assumed would be too high. The error in this case would be represented by the oxygen in the amount of the base $Ag_2O$ added to the flask during the experiment, *i.e.*, 16/232 of 0·13 mg. If, on the other hand, the increase in weight arises from the formation of silver silicide in the reducing atmosphere (hydrogen), the weight of silver would be too low by the amount of oxygen removed from the silica; this would be in the proportion 32 : 400 of the increase. In neither case would it have an appreciable effect on the results.

*Other Values for the Atomic Weight of Carbon.*

Modern values of interest are the following: 12·003 (from the density of carbon monoxide; Leduc; Rayleigh); 12·003 (from the density of methane; Baume and Perrot); 12·017 (from the ratio of tetraethylammonium bromide to silver, and to silver bromide; Scott); *12·005 (from the ratio of sodium carbonate to silver and to silver bromide; Richards and Hoover).

The older results, obtained by the combustion of carbon in oxygen, have been corrected by Scott for the alteration in volume of the potash solution on absorption of carbon dioxide (J. 1897, **71**, 550). Thus revised, the values become: 11·9938 (Dumas and Stas); 12·0054 (Erdmann and Marchand); 11·9973 (Roscoe); 12·0056 (Friedel); 12·0018 (van der Plaats).

The mean of these (12·001) is very close to the whole number, whereas that of the former, 12·007, obtained by very different experimental methods, is distinctly higher.

*The Present Position of the Atomic Weight of Silver.*

The unique position held by silver among the elements, as the link by which the atomic weights of so many of them are related to the oxygen standard, demands that its own value should be fixed within the narrowest possible limits. Stas established his value for silver (107·93) in relation to oxygen by an indirect method. He first found the ratio of potassium chloride to oxygen in potassium chlorate, and then the weight of silver required to react completely with pure chloride. His results by this method having been rejected, there are few data on which to base a new value. The modern one—107·88—rests mainly on the determination of two ratios—nitrogen to oxygen, and silver to silver nitrate. Since a direct comparison of silver with oxygen is not possible, owing to the instability of the oxide, this is the best method at present available. The atomic weight of nitrogen is certainly one of the most accurately known, and the ratio of silver to silver nitrate has been ascertained by Richards and Forbes with an exactness which would seem to be final. After an exhaustive examination, both of the silver and the nitrate obtained from it, and allowing for slight decomposition of the nitrate on fusion, and retention of water and ammonium nitrate before, they estimated the ratio $Ag : AgNO_3 = 100 : 157{\cdot}479$. Assuming only that $N = 14{\cdot}008$ when $O = 16$,

$$Ag = 107{\cdot}879.$$

Stas conducted similar experiments in his attempts to find the

* According to Moles (*J. Chim. Phys.*, 1917, **15**, 51), if the Harvard value for silver (107·871) be accepted, Na = 22·993, and from Richards and Hoover's work, C = 12·000.

atomic weight of nitrogen. He assumed that his high silver value was established and so deduced a high value for nitrogen (14·04). It is interesting to compare his actual ratio $Ag : AgNO_3$ with that above, and, reversing his reasoning, use it to find the silver value.

He carried out two series of measurements, one published in 1860, the other in 1865. In each he obtained two numbers, one for the nitrate heated below fusion, the other—lower—after actual fusion.

| | $Ag : AgNO_3$ | |
|---|---|---|
| First Series. | 100 : 157·4857 (unfused). | Ag = 107·867 |
| | ·472 (fused). | 107·893 |
| Second Series. | ·4952 (unfused). | 107·849 |
| | ·484 (fused). | 107·870 |

If we reject the first series on the ground that the later experiments, conducted with purer silver, are more trustworthy, and the first result of the second series because the unfused nitrate retains traces of volatile matter, we are left with the fourth value, depending on two experiments only. It happens to coincide with the mean of the other three.

$$Ag = 107{\cdot}870.$$

The ratio Ag : AgCl might also be used to deduce the atomic weight of silver. No ratio has been measured so often, and certainly none with greater care. Provided the atomic weight of chlorine is accurately known, we should be able to get valuable confirmation of that of silver.

If we accept the number 35·460, based on the synthesis of hydrogen chloride and its volume composition, and the ratio Ag : AgCl as 100 : 132·867 (Richards and Wells),

$$Ag = 107{\cdot}889.$$

Unfortunately, the atomic weight of chlorine used has not been obtained by direct reference to oxygen, but indirectly from its ratio to hydrogen. To get it in terms of oxygen, the ratio of oxygen to hydrogen has to be used. It is therefore affected by two experimental errors. When these are added to the error of the actual ratio Ag : AgCl, the value for silver deduced is too uncertain to be used for comparison with the nitrate value. Brauner has shown that the Ag : AgCl ratio can be used with greater advantage to obtain the atomic weight of chlorine on the basis of the accepted value for silver. The uncertainty then involved is only $\frac{1}{10}$th of that in the former case.

There are several modern determinations of the value for silver, which, although indirect, do not require the knowledge of another atomic weight. First among these we have the value obtained by Richards and Willard (*J. Amer. Chem. Soc.*, 1910, **32**, 4) in their work on "The Atomic Weight of Lithium." Their method of

deducing the atomic weight of silver is very similar to that of Stas. The ratio LiCl : $LiClO_4$ was first determined, then the ratio Ag : LiCl. Their result was

$$Ag = 107{\cdot}871.$$

Baxter and Tilley (*ibid.*, p. 1591) reduced iodine pentoxide to hydrogen iodide, converted this into silver iodide, and so found the ratio AgI : $I_2O_5$, and finally Ag : I.

$$Ag = 107{\cdot}864.$$

Scheuer (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 381) treated a weighed amount of silver with pure sulphuric acid, condensed the sulphur dioxide in liquid air, and weighed both it and the silver sulphate.

$$Ag = 107{\cdot}884.$$

From the ratios AgCN : Ag, and AgCNO : Ag,

$$Ag = 107{\cdot}871.$$

It is interesting that most of the work summarised above points to a lower value than the rounded number 107·88. Richards, in "Atomic Weights and Isotopes," favours the figure 107·872—about 1 part in 10,000 lower. Before acknowledging that this is the limit of accuracy possible with modern methods and appliances, it is desirable that silver should be compared with other elements (or groups) whose atomic weights are directly referable to that of oxygen.

During the progress of the work described above, I have been encouraged and helped by the advice and criticism of Dr. A. Scott and Professor S. Smiles. To them I am deeply grateful. The expense of the materials and silica apparatus has been largely met by grants from the Research Fund Committee of the Chemical Society.

WEST HAM MUNICIPAL COLLEGE. [*Received, July 8th*, 1924.]

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# NOTES.

*The Behaviour of the Simple Halides with Water.* By NEVIL VINCENT SIDGWICK.

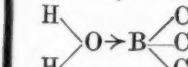
WATER can form a co-ordinate link (a non-polar link of two shared electrons, both taken from one of the two linked atoms), either by the oxygen contributing, or by the hydrogen taking up, the necessary pair of electrons. In $H_4O_2$ or $H_6O_3$ both processes occur, giving $H_2O{\rightarrow}H{-}O{-}H$ (the arrow pointing at the atom which receives the two electrons).

It has been suggested (Sidgwick, *Trans. Faraday Soc.*, **1923**, **19**, 469; Sidgwick and Callow, J., 1924, **125**, 532) that the maximum covalency of an element depends on its position in the periodic table, being 2 for hydrogen, 4 for the first short period (Li–F), 6 for the second (Na–Cl), and probably the whole of the first long period (K–Cu–Br), and 8 for the elements from rubidium onwards (I originally suggested that 8 became possible after nickel, but there is evidence that it does not begin before rubidium).

These assumptions will explain the diverse behaviour of the simple halides with water, which is either (1) ionisation, or (2) hydrolysis (more or less complete) thus : $-XCl \longrightarrow -XOH + HCl$, or (3) no reaction, or (4) hydrolysis thus : $-XCl \longrightarrow -XH + HOCl$.

(1) Ionisation. The loss of successive electrons from an atom becomes increasingly difficult as the ion becomes more positive. Anything which diminishes the positive charge on the ion will make it easier. When an ion hydrates, the oxygen of each water molecule shares a pair of its electrons with the metal; these electrons must enter in some way into the metallic atom, and so must give it some negative charge. Hence hydration should facilitate ionisation, and the more so the more water molecules are added. We should thus expect to get ions of a higher valency when they can take up 6 water molecules than when they can only take up 4. This is what happens. Where the maximum covalency is 4 we get uni- (Li) and bi-valent (Be) cations, but not tervalent (B); where it is 6, we get tervalent (Al) as well. Quadrivalent cations are not found until we reach the elements with a maximum covalency of 8, as with the stannic ion.

(2) When ionisation is no longer possible, the water will tend to attach itself to the molecule, and then react with the halogen. In $BCl_3$, for example, the incomplete octet of the B completes itself by sharing a pair of electrons from the O of the water, giving



; the H then reacts with the Cl, giving HCl and ultimately boric acid. The same happens with $SiCl_4$, because though the Si has completed its octet, it can expand this to 12 (covalency 6), and so can take up two water molecules in this way. It happens also with $PCl_3$, $PF_5$, $IF_5$, and the halides of the heavier elements as a rule when they do not ionise.

(3) $CCl_4$ is in a different case. It cannot ionise : it has a complete octet, and cannot increase it. So it cannot attach a water molecule at all, and hence does not react. This accounts for the very remarkable stability of $CCl_4$ and of the halogens in the substituted hydrocarbons. $SF_6$ and $SeF_6$ are in the same position;

they are exerting their maximum covalency, and cannot take up a water molecule; accordingly, they are as inactive as $CCl_4$, and are not acted on even by hot alkali. But the hexahalides of the elements heavier than rubidium are all hydrolysed by water to give HCl: $MoF_6$, $TeF_6$, $WF_6$, $WCl_6$, $UF_6$. $OsF_8$ is also hydrolysed, which perhaps indicates a maximum covalency of 10 for the elements of highest atomic number.

(4) $NCl_3$ (and also $OCl_2$) is in a different position again. Its actual covalency is 3, and so it can form another non-polar link; but its octet is already full, and cannot expand. Hence it cannot take up a pair of electrons from the oxygen of the water; but it can, and no doubt does, offer its own unshared pair to the hydrogen of the water, giving $Cl_2N\swarrow^{Cl}_{H-O-H}$. The chlorine now reacts, not with the hydrogen, but with the hydroxyl, giving hypochlorous acid, whilst the other hydrogen remains attached to the nitrogen.—DYSON PERRINS LABORATORY, OXFORD. [*Received, November 13th*, 1924.]

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*The Influence of Nitrogen Dilution on the Speed of Flame.* By OLIVER COLIGNY DE CHAMPFLEUR ELLIS.

WITH regard to recent papers under this heading (Campbell and Ellis; Ellis and Stubbs, this vol., pp. 1957, 1960), the authors wish to point out that the speed of flame in their experiments, if proportional to one additive constant of the constituent gases of the mixtures employed, must be proportional to any other; they used the calorific value as the constant, because figures are available for completely combustible mixtures and provide a convenient common denominator for different fuels. Thermal conductivity, however, is not accurately additive. The authors regret that they overlooked results which show other relationships with respect to the "uniform movement" of flame in W. Payman's paper on "The Propagation of Flame in Complex Gaseous Mixtures" (J., 1920, **117**, 48).

Dr. Colin Campbell and Mr. Sydney Robert Stubbs desire to associate themselves with this statement.—SAFETY IN MINES RESEARCH BOARD EXPERIMENTAL STATION, SHEFFIELD. [*Received, November 12th*, 1924.]

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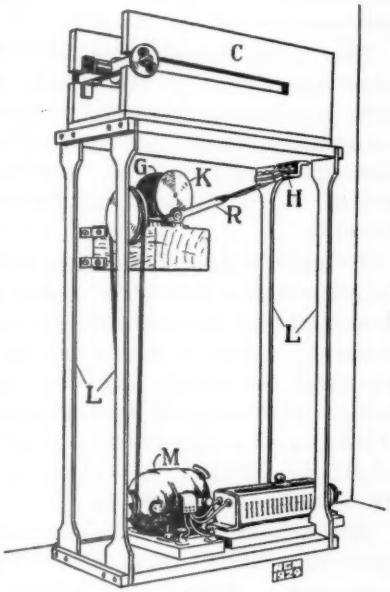
*A Trustworthy Shaking Machine.* By ARTHUR GEORGE MILLIGAN.

A SOURCE of trouble common to most reciprocating bottle-shaking machines, which may be called upon to run continuously and unattended for long periods, is the severe strain of stopping and

reversing the moving carriage and its load at each end of the stroke. It entails excessive wear on the gears and bearings; it is particularly hard upon belt-drives; and the danger of stoppage on a dead point can be overcome only by the use of power disproportionate to the actual work to be done and a flywheel disproportionately large and heavy.

The defect has been remedied in the shaker here illustrated, the credit for whose design is due principally to Mr. C. Menkens. The bottle-carrier, C, is supported upon four springy laths, L, of straight-grained ash which allow it a limited horizontal displacement while exerting a strong restoring force at each end of the stroke. If the period of the stroke approximates to the natural period of free vibration, very little power is required for shaking and the strain upon the transmission is negligible.




The driving mechanism is of subsidiary importance: in this instance it comprises a 1/16 h.p. electric motor, M, a worm reduction gear, G, mounted on a wall bracket, a crank, K, and a connecting rod, R, attached to the carrier by a stout leather hinge, H, which contributes largely to the silent running of the machine.

The whole apparatus is neat and compact, stands a convenient height (3 feet) above the floor, and is quiet and very trustworthy in action.—[*Received, October* 11*th*, 1924.]

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*The Orientation of Derivatives of Triphenylphosphine Oxide.* By Frederick Challenger and John Frederick Wilkinson.

Michaelis and Soden (*Annalen*, 1885, **229**, 324) nitrated triphenylphosphine and its oxide, obtaining a trinitrophenylphosphine oxide, m. p. 242°. They considered this to be the para-compound, whilst a resin, m. p. 66—68°, was regarded as the ortho-derivative.

We have confirmed the formation of the compound, m. p. 242°, but have not obtained an isomeride, either from the phosphine or its oxide. Extraction of the crude products with alcohol gave

low-melting solids which, on further nitration, yielded the trinitrophenylphosphine oxide, m. p. 242°. No other product was isolated.

From the trinitro-derivative, Michaelis and Soden obtained the triamino-compound. By the diazo-reaction, we prepared the trichloro-derivative, which did not depress the m. p. of the tri-*m*-chlorophenylphosphine oxide obtained from phosphoryl chloride and magnesium *m*-chlorophenyl bromide. The trinitrophenylphosphine oxide, m. p. 242°, is therefore a meta-compound, as was to be expected.

*Preparation of Trichlorophenylphosphine Oxide by Diazotisation.*—Triamino-derivative 4 g., hydrochloric acid 30 c.c., water 20 c.c., sodium nitrite 10 g. at − 5°. Cuprous chloride from 8 g. of copper carbonate.

The product was extracted with hot light petroleum, and the resulting solid recrystallised from dilute alcohol and from benzene-light petroleum; m. p. 135°. The m. p.'s of mixtures of this oxide with tri-*m*-chloro- and with tri-*p*-chloro-phenylphosphine oxide were 135° and 119—123°. 0·1563 gave 0·1760 AgCl; 0·1017 gave 0·1142 AgCl. Cl = 27·86, 27·79. $C_{18}H_{12}OCl_3P$ requires Cl = 27·89 %.

*Tri*-m-*chlorophenylphosphine Oxide.*—Phosphoryl chloride (1·5 g.) in ether was added to a cooled solution of magnesium (0·96 g.; 4 atoms) and *m*-chlorobromobenzene (8·6 g.; 4 mols.) in ether-benzene. After 2 hours on the steam-bath, the solvent was removed, ice added, and the product purified as before, giving felted needles from light petroleum, m. p. 135°. 0·1632 gave 0·1832 AgCl; Cl = 27·76. 0·1472 gave 0·3054 $CO_2$ and 0·0424 $H_2O$; C = 56·59; H = 3·20. $C_{18}H_{12}OCl_3P$ requires C = 56·63; H = 3·17; Cl = 27·89 %.

*Tri*-p-*chlorophenylphosphine oxide* was similarly prepared and purified. Except in m. p. (174°), it closely resembles the meta-compound. 0·1998 gave 0·2256 AgCl; Cl = 27·91. 0·1838 gave 0·3808 $CO_2$ and 0·0510 $H_2O$; C = 56·50; H = 3·09. $C_{18}H_{12}OCl_3P$ requires C = 56·63; H = 3·17; Cl = 27·89 %.—The University, Manchester. [*Received, October 25th,* 1924.]

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*Spontaneous Combustion of Ethylene during the Preparation of Ethylene Dichloride.* By Ram Krishen Sharma.

During the preparation of ethylene dichloride by passing purified ethylene into chlorine water, even at a temperature below 15°, a periodic flash was observed at the point where the delivery tube entered the solution. The combustion of ethylene left in the liquid small quantities of very finely divided carbon.—Forman Christian College, Lahore, India. [*Received, September 22nd,* 1924.]

# OBITUARY NOTICES.

## GEORGE HERBERT BAILEY.

BORN MAY 17TH, 1852; DIED APRIL 18TH, 1924.

GEORGE HERBERT BAILEY, second son of John Joseph Bailey, was born May 17th, 1852, at Barnard Castle in Teesdale, where his father was headmaster of the old National School. Apprenticed at the early age of 13 as a pupil teacher in his father's school, the boy seized every opportunity for acquiring knowledge, and he was lucky to find in his native town enthusiasts such as Mr. Heslop, who taught him Greek and Latin, Mr. Maughan, who taught him Botany, and above all Canon Brown, the Vicar, who introduced him to practical chemistry. Perhaps the strongest influence came a year or two later from the teaching of Mr. W. Gunn, of the Geological Survey, under whose advice he studied mechanical drawing at the classes held in the Mechanics Institute.

Bailey was not yet 23 when he was appointed headmaster of the Grammar School in the neighbouring town of Bowes, and during the five years he held this position he not only conducted science classes in the evening at Barnard Castle, but he continued his own studies which he supplemented by vacation courses at University College, London, and at South Kensington. He graduated B.Sc. in the University of London in 1878, taking Honours in Physical Geography and Geology.

In 1880, Bailey was appointed Science Master at Tettenhall College, near Wolverhampton; he resigned this position in 1882 to enter the Owens College, where he worked under Professor Roscoe in the Chemical Laboratories and under Dr. Schuster on spectroscopy in the Physical Department. His first research was published in the Society's Journal in 1884; in this he describes the preparation of the metavanadates of methylamine, ethylamine, and dimethylamine; he also obtained large crystals of tetramethylammonium metavanadate.

Elected Dalton Chemical Scholar, he spent the session 1884–5 at Heidelberg under Bunsen, to whose laboratory so many Owens students were sent by Roscoe. In carrying out the analysis of koppite, a mineral rich in niobium, Bailey found that zirconium could be separated completely from the oxides of titanium, niobium, and iron by means of hydrogen peroxide in an acid solution. Clève had obtained in the same year a peroxide of

zirconium, to which he assigned the formula $ZrO_3$, by adding ammonia and hydrogen peroxide to a solution of the sulphate. Bailey showed that the pure peroxide had the formula $Zr_2O_5$ and its precipitation in acid solution was an easy way of separating and estimating zirconia. This work appeared in the Journal in 1886.

Returning to Manchester with the Heidelberg degree, he gained the London D.Sc. degree and was appointed Demonstrator and Assistant-lecturer in the Owens College.

When Sir Henry Roscoe resigned the Chair of Chemistry in 1886, a large share of the teaching and of the organisation of the laboratory classes fell to Dr. Bailey, to whose ability, hard work, and loyalty the writer owed much in his early years at Manchester; for Dr. Bailey was not only a good teacher, he knew the nature of the north-country students, he joined in their sports and was welcomed at their social meetings. In spite of his many routine duties, he always found the time and energy to keep two or three advanced students busy on some research in which he had interested them. Thus during the first ten years of his lectureship at Owens Bailey presented to the Society a number of papers describing investigations conducted either alone or in conjunction with students. Of these there may be mentioned his work on the stability of the sulphates of the dyad metals when heated; on the stability of metallic oxides at very high temperatures (he prepared $Cu_3O$ by heating CuO above the melting point of platinum); on the reactions of the halogen acids with phosphorus pentoxide; on the volatilisation of salts during evaporation. Perhaps his most ambitious work was that undertaken with Dr. Thornton Lamb on the preparation of pure palladium salts with the object of determining its atomic weight. They found that palladammonium chloride could be prepared in the pure state and the yellow crystals could be reduced in a current of hydrogen at a red heat, leaving the metal in a coherent mass. The mean of their results gave Pd 105·5 when H = 1.

Dr. Bailey's interest in gardening led him with other members of the Manchester Field Naturalists' Society to undertake a systematic examination of the pollution of the atmosphere in the city and suburbs. He devised an automatic apparatus for determining the acid present in the air, and with it comparative tests were made at the Owens College and at the Town Hall. He also experimented on the action of daylight in decomposing a solution of hydrogen iodide, and had daily light-tests made in and around the city. In addition the leaves of plants (chiefly *Aucuba*) were collected and the deposit on them analysed. The general conclusions reached

after two years' work were that the closely-packed residential quarters were more polluted with acid and "blacks"—arising from domestic fires—than the business portions of the city, and that the more distant suburbs of large industrial towns in the north receive about one-third the active sunshine that falls on a southern seaside town.

In 1909, after serving on the staff of the Owens College and the Manchester University for 24 years, Dr. Bailey was appointed Chief Chemist to the British Aluminium Company. His headquarters were at Kinlochleven, Argyllshire, where he enlarged the laboratories and was mainly responsible for the design of the research laboratories. Here he simplified the routine analytical methods, and pursued investigations on many problems arising in the manufacturing processes carried out not only at Kinlochleven, but at the other works of the company in Great Britain and Norway, to which he paid frequent visits. Dr. Bailey held this appointment until the end of 1920, when he retired, but he retained the position of Consulting Chemist to the company until his death. Mr. W. Murray Morrison, Technical Director of the company, writes: "It is impossible for me to speak too highly of the value of Dr. Bailey's work to 'British Aluminium,' and of the extremely happy and pleasant association which I and my staff had with him for so many years. It was a real pleasure to work with one so keen, practical and energetic." All those who have worked with Dr. Bailey will feel that Mr. Morrison has happily described the character of the man.

On his retirement, although still keeping up his connexion with the company and advising them on new processes, Dr. Bailey devoted himself to his old hobby of gardening. He settled at Staines, but removed early this year to a small property he had purchased at Datchet, where he seemed to be enjoying good health and spirits. On February 8th last, he delivered an interesting lecture on the "Production and Properties of Aluminium" at the Sir John Cass Institute. On Good Friday, April 18th, he was at work in his garden when the end came suddenly by heart failure. He was buried in the quiet country cemetery at Datchet. He left a widow, a daughter, and three sons: the last have chosen adventurous careers, one is a Squadron-leader in the Royal Air Force, a second is in Rhodesia, the third in New Zealand.

H. B. D.

## SURENDRA NATH DHAR.

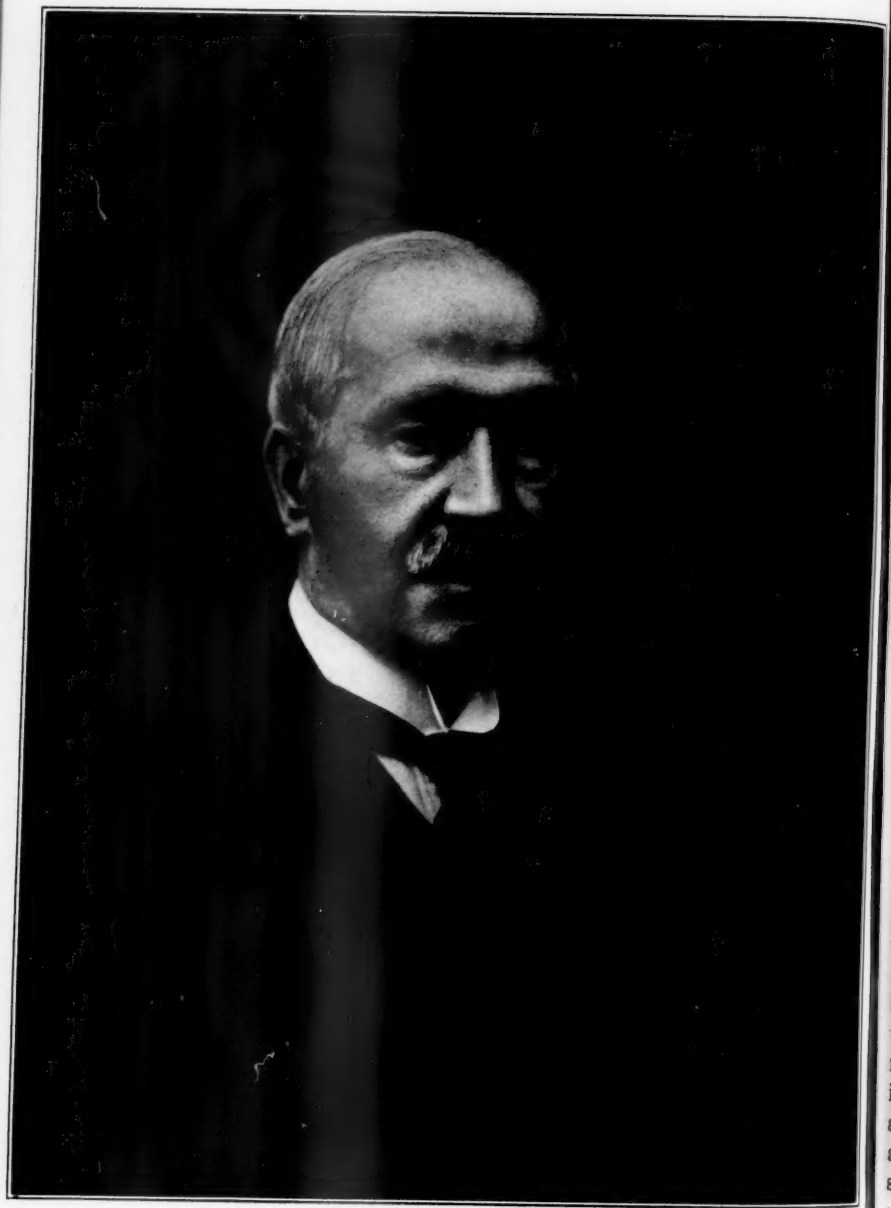
BORN JANUARY, 1892; DIED DECEMBER 9TH, 1923.

SURENDRA NATH DHAR was born in January, 1892, in a village in the Moulvibazar sub-division of the district of Sylhet in Assam. He received his early schooling in the village "Pathsāla" and later in Murarichand school at Sylhet. In 1909, he passed the entrance examination of the University of Calcutta and became a ward of Sir Prafulla Chandra Rây. Studying first at the Ripon College and later at the Berhampore College, he completed the courses for the intermediate and final B.Sc. examinations; in the latter, he was placed in the first division with honours in chemistry.

Dhar's post-graduate studies commenced in 1913 at Dacca under Dr. E. R. Watson (now Principal of the Technological College at Cawnpore) and he obtained the M.Sc. degree (first class) in 1915. It is at this time he was initiated into research work on the xanthone series by Dr. Watson. As Assam Government Scholar, he carried on research work at the Presidency College, Calcutta, for two years. He was then appointed Professor of Chemistry at the A. M. College, Mymensingh (Bengal) and, three months later, Guru Prasanna Ghose Scholar of the Calcutta University. On the recommendation of the Government of Assam, the scholarship of the Government of India was awarded to him. With these two scholarships, Dhar left for England in September, 1918. He entered the Imperial College of Science and Technology, London, where, under the able guidance of Professor J. F. Thorpe, he continued his work on the xanthone series. After a year's work, he was admitted to the D.Sc. Degree of the London University. He spent a year in touring the Continent, and then, after working for some time on colours at the Badische Anilin- und Soda-Fabrik, returned to India. In July, 1921, he entered the Indian Educational Service and was appointed Professor of Technical Chemistry at the Civil Engineering College, Guindy, Madras.

Here, unsupported, and hampered by the difficulties attending retrenchment, Dhar laboured to improve the condition of the chemical department. Here also, on December 9th, 1923, occurred his tragic death, due to the inadvertent inhalation (or tasting?) of potassium cyanide fumes.

Dhar leaves behind an old mother, a young wife—he was married, only in June, 1923, to Miss Nanda Rani Sinha—and a large circle of friends and co-workers at Madras and Assam. Whatever might have been his rank as a chemist, his place as a man is assuredly very high. He wanted to infuse others with the spirit of research and to disseminate knowledge. His maxim was:—"No one for



JAMES JOHNSTON DOBBIE.

[*To face Trans., p.* 2681]

himself alone; all for all and every one for others." He was intensely religious and a splendid example of plain living and high thinking. Simple in habits, unostentatious in manner, diligent in study, and careful in his work, he gave promise of a great career, which the cruel hand of death has brought to an untimely end. An affectionate son, a loving friend, and a dutiful man, his like it will not be easy to find.

T. S. NATRAJAN.

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## JAMES JOHNSTON DOBBIE.

BORN AUGUST 4TH, 1852; DIED JUNE 19TH, 1924.

AT Fairlie, on the Ayrshire coast, in the home which had been his since boyhood, there passed away in Sir James Dobbie one who had endeared himself alike to the village community and to the wider fraternity of scientific men.

The son of Alexander Dobbie, scientific and nautical instrument maker, James Johnston Dobbie was born in Glasgow in 1852, and received his first education privately and afterwards at the High School of Glasgow. On his mother's side he was related to David Wilkie the artist, and something more than mere coincidence may have entered into his early choice of Architecture as a career. In the three years during which he pursued this calling, he attended the Humanity classes in the old buildings of the University of Glasgow. His love of academic learning overcame his original predilection, and he embarked on a complete arts course as a student of the University at Gilmorehill, taking out classes in Philosophy, Classics, English Literature, Mathematics, and Natural Science. In the fourth year of his arts studies he began to attend medical classes, combining anatomy and physiology in his course for a science degree at Edinburgh, there being at that time no science degree at Glasgow. At the age of 22, he graduated M.A. with first class honours in Natural Science and, shortly after, was awarded the Geo. A. Clark Scholarship of the value of £200 a year tenable for four years. At the University of Edinburgh he came under the influence of Professors Blackie, Crum Brown, and Archibald Geikie, and, at 26, won first place in order of merit at the B.Sc. examination and was nominated to the Baxter Scholarship. He also spent two semesters at Leipzig, attending lectures in Philosophy and Physics, working in practical Chemistry under Kolbe and Wiedemann, and in Mineralogy under Zirkel. He gained the D.Sc. of Edinburgh in 1879 by a Thesis on Quinine.

His career as a student had been a distinguished one both in Glasgow and Edinburgh. Prof. A. Geikie in a letter to his former

student wrote, in 1884, "The position you took in my class in the Edinburgh University gave me confidence that you could not fail to attain eminence in any department in which you applied the abilities and industry with which you worked with me at Geology"; whilst Edward Caird, Professor of Philosophy at Glasgow and afterwards Master of Balliol, wrote that he was "much impressed by the maturity of thought and power of expression" he had gained.

Earlier he made the aquaintance of William Ramsay, who had just returned from Germany, and from Ramsay he obtained assistance in reading organic chemistry for the first time from Schorlemmer's "Chemistry of the Carbon Compounds." This aquaintance ripened into close friendship, and the two men joined in a research on the constitution of quinine, quinidine, cinchonine, and cinchonidine, little being known up to that time as to the structure of alkaloids. They proceeded to oxidise these natural products with permanganate in alkaline solution and isolated pyridine-tricarboxylic acids. This was the first occasion that the essential connexion between pyridine bases and the alkaloids was recognised. Two papers on this subject by Ramsay and Dobbie appeared in the *Journal* in 1878 and 1879. In the latter year a similar observation was made in the *Berichte* by Hoogewerff and van Dorp.

In the cellars of the laboratory at Glasgow were stored the fractions collected by Prof. Anderson during his distillation of bone oil. Ramsay, as Assistant in the Department, had access to these products and gained familiarity with the smell of pyridine. It was owing to this circumstance that the two workers were able to detect so readily the presence of pyridine when the silver salts of the pyridinetricarboxylic acids were ignited, and to this olfactory origin may be traced the success of Dobbie's first essay in research, determining possibly the choice of his life work on the alkaloids.

During the tenure of the Clark Scholarship, Dobbie had inaugurated at the University a course of lectures on mineralogy which was largely attended. As the University did not possess the necessary apparatus for teaching the subject, he equipped the class at his own cost with the instruments and specimens needed for the purpose of practical instruction. Shortly afterwards, he was appointed Assistant on the staff of the chemistry department at Glasgow in succession to Ramsay, who had been elected to the Chair of Chemistry at Bristol. Dobbie's duties were to take charge of tutorial classes in Chemistry under Prof. Ferguson, who had succeeded Prof. Anderson, and to take general control of the laboratory.

On many occasions the two friends indulged their fondness for walking expeditions, some reference being given in Dobbie's own reminiscences of Ramsay in the biography written by Sir William Tilden. Together Dobbie and Ramsay climbed many of the peaks in the Highlands; they visited Norway and spent many weeks rock-scrambling on the shores of the fjords collecting mineral specimens. It was characteristic of the man that these and other excursions, undertaken from sheer love of scenery and excitement of travel, yielded several papers for the geological magazines: (1) on the occurrence of Euxenite and other rare minerals in veins of graphic granite at Hittero, Flekkefjord, Norway (1879); (2) on the composition of Euxenite (1881); (3) on a specimen of altered Dolomite limestone (1881); (4) on a new variety of Saponite (*Mineralogical Mag.*, 1882). The interesting collection of Norwegian minerals was afterwards given to University College, Bangor, and on one occasion later, when they were requisitioned by Ramsay for his detailed search for rare gases, one mineral specimen yielded him the desired result.

At this time Dobbie took an active part in founding the Glasgow and West of Scotland section of the Society of Chemical Industry and became its first secretary. As such he served on the council of the Society and came into close touch with leading industrial chemists in Scotland and also in London. One result of this association was a patent (1882) by J. J. Dobbie and J. Hutcheson on a new process of bleaching. The process was based on the electrolytic production of chlorine from brine, the cloth wetted with brine being passed between rollers conducting the current. Other papers contributed about this time were on the formation of serpentine from dolomite limestone (conjointly with G. G. Henderson) and on the red resins known as dragon's blood, by the same authors. A paper on the relation between the electrical qualities and chemical composition of glass was published with Thomas and Andrew Gray in 1884, in the *Proceedings of the Royal Society*, a subject to which Dobbie returned in 1899.

After competing unsuccessfully for the Chair of Chemistry in the newly-established University College at Dundee, Dobbie was elected in 1884 to the Chair of Chemistry and Geology at the University College of North Wales, Bangor, which had just been founded. Although Geology was joined with Chemistry in the appointment, he never gave any systematic courses in the subject, but only occasional lectures. It was soon recognised that the duties attending the direction of the Department of Chemistry were sufficient to engage the whole time of one man. His first task at Bangor was to plan and supervise the conversion of the old coach-houses and

stables of the Penrhyn Arms Hotel, which had been acquired, into lecture rooms and laboratories. This was contrived so skilfully, although at very little cost, that the accommodation and arrangements provided have continued to serve the purpose to which they were adapted.

Among Dobbie's colleagues at Bangor in charge of other subjects were young men of conspicuous ability: H. R. Reichel (Principal), E. V. Arnold, W. Rhys Roberts, Henry Jones, Andrew Gray and C. B. Mathews. The task which confronted them was no easy one. The financial endowment was meagre, but the pioneer work of these men received the generous support of the people of North Wales, whose devotion to the College cannot be commended too highly. A popular lecture by Prof. Dobbie on the relation of Chemistry to Agriculture led to repeated demands from farmers to hear him. The interest spread to other parts of Wales, and he continued to give similar lectures, until the enthusiasm developed into a movement into which Dobbie threw himself wholeheartedly. To bring science to the door of the agriculturists, and, what he greatly valued, to bring agriculturists to the College and to establish a centre of agricultural education, were his aims and ultimately his achievements. He spent vacations on the Continent, chiefly in Denmark, studying methods of agricultural education, opened a campaign to solicit funds from the land-owning classes and farmers, started centres for training in dairying, gave lectures and conducted field experiments on the use of fertilisers, expending his energies throughout the whole countryside even so far south as Montgomeryshire.

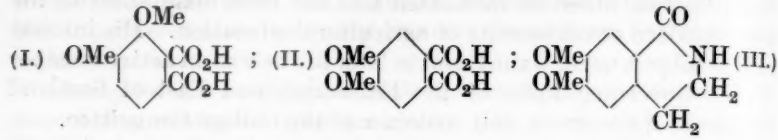
Dobbie's inborn gifts as an administrator received the fullest exercise, and his unfailing tact and charm of personality combined to create an atmosphere of complete sympathy on all sides with his scheme. At that date there was no Board or Ministry of Agriculture, but Dobbie saw an opportunity to solicit the interest of the State. An Agricultural Committee of the Privy Council had just been charged with the allocation of very limited funds for agricultural purposes. He interviewed the Committee, explained the extent to which his schemes of education had been successful, and to him was awarded the first grant ever given for Agricultural Education. Year by year this grant was increased, and it became possible, in 1889, to provide a complete course of instruction at Bangor leading to a Diploma, and later to a Degree, in Agriculture. Thus was established the first Agricultural Department in connexion with a University or University College in England and Wales. In a few years' time the scheme was copied by University Colleges in Leeds and Newcastle, and the movement spread. Dobbie always emphasised the importance of a training in the pure sciences, to the

standard of a degree in science, as a preliminary to specialisation in agricultural subjects proper, and to the end of his life regretted that this principle which he inculcated had not been maintained in the more modern developments of agricultural education. His interest in this subject never waned, and in later life he was an active member of the Governing Body of the Edinburgh and East of Scotland College of Agriculture, and convener of the College Committee.

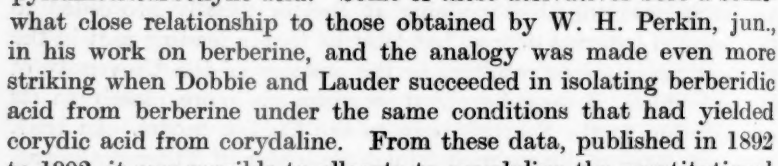
In these preliminary years at Bangor no one worked more assiduously to bring the College into prominence, but his public activities did not impair the conscientious performance of his work as a teacher in his department, which was always his first care. Students receiving their training at Bangor usually proceeded to the London external degree, but later he took a leading part in the difficult negotiations resulting in the creation of the University of Wales, which, it may be noted, corresponds more closely in its constitution to the Scottish than to the English model. In 1887, while at Bangor, he married Violet, daughter of Thomas Chilton, Esq., J.P., of Gresford near Wrexham, and of Liverpool.

It soon became possible again to devote attention to original investigations, and his mind naturally returned to the topic, albeit a difficult one, of his doctorate thesis, namely, the alkaloids. Other workers were meanwhile engaged on quinine, so that he determined to break fresh ground and undertook the study of the alkaloids of *Corydalis cava*. Of the five alkaloids present in the tubers, Dobbie and his assistant, A. Lauder, isolated three: corydaline, corybulbine, and corytuberine. The second of these was readily transformed into the first by synthetic methods, and it is with corydaline that Dobbie's name will always be associated. Earlier workers had failed to effect a complete separation of this alkaloid from its congeners, and the obvious step was to devise a means to this end and determine the molecular formula by analysis of the pure substance and its salts. This was no easy task, since solutions of the alkaloid were peculiarly sensitive to heat and light. The formula, $C_{22}H_{29}O_4N$, at first ascribed to corydaline, was afterwards modified to one containing two hydrogen atoms less. Mild oxidation changed the colourless base to a coloured one by loss of four hydrogen atoms, and this compound, dehydrocorydaline, was shown to be closely related to berberine, the absorption spectra of the two substances being almost identical. Similarly, tetrahydroberberine was found to be related intimately to corydaline, but the latter contained four methoxyl groups and the former only two. Oxidation with permanganate yielded both hemipinic acid (I) and *m*-hemipinic acid (II), thus indicating the presence of two benzene nuclei in the alkaloid. Using cold permanganate another product,

corydaldine (III), was also isolated and shown to be a derivative of *iso*quinoline.



On the other hand, a degradation product obtained by oxidation with nitric acid was corydic acid (IV), which, with permanganate, was converted successively into corydilic acid (V) and α-methylpyridinetricarboxylic acid. Some of these derivatives bore a somewhat close relationship to those obtained by W. H. Perkin, jun., in his work on berberine, and the analogy was made even more striking when Dobbie and Lauder succeeded in isolating berberidic acid from berberine under the same conditions that had yielded corydic acid from corydaline. From these data, published in 1892 to 1902, it was possible to allocate to corydaline the constitutional formula (VI):



(IV.) (V.) (VI.) *Corydaline.*

Impressed with the utility of absorption spectra data as a guide to the solution of problems of constitution, Dobbie joined with W. N. Hartley in developing this line of inquiry which had been originated in 1852 by Sir G. G. Stokes. Alongside the constitutional work on corydaline these investigations were also vigorously prosecuted. Numerous papers appeared, first by Hartley and Dobbie and then by Dobbie alone, or with A. Lauder and C. K. Tinkler, involving the measurement of the absorption spectra of a large and varied selection of organic compounds. These results were also embodied in a series of five reports for the British Association in 1899—1903. Briefly summarised, the salient features of this work may now be given.

The types of compounds exhibiting absorption bands or showing selective absorption have the valency bonds arranged as in benzene. Selective absorption was exhibited also by compounds containing residues such as those of pyridine and pyrazine which simulate the benzenoid structure. Conversely, no absorption bands were

shown by members of the furan, pyrrole and thiophen groups, or by diketohexamethylene or the polymethylenes. So sensitive is the method of photographing spectra that it was easy to detect the presence of 0·00014 % of pyridine in commercial ammonia.

Dobbie regarded the method as ancillary to the usual procedure of determining constitution by chemical processes, and found it invaluable as a means of confirming conclusions reached by the ordinary methods employed by chemists. Accepting these limitations, he proceeded to use absorption spectra measurement with a success which was largely determined by his choice of particularly apt examples. The chemical behaviour of methyl*pseudo*isatin clearly indicated its lactam structure, whilst methylisatin was the lactim. The absorption spectra curve of the parent substance, isatin, was identical with that of the former compound and totally different from the latter, and therefore to isatin was ascribed the lactam structure. Analogous conclusions were drawn regarding carbostyril, *o*-oxycarbanil, and cyanuric acid. Phloroglucinol showed a selective absorption similar to its trialkyl ether and consequently possessed the benzenoid structure.

The study of tautomeric change was continued with the three isomerides (out of a possible thirteen) of dibenzoylsuccinic ester isolated by Knorr in 1896. The β- and γ-esters were known to be different keto-forms, and the α-ester was thought to be enolic. The absorption curves of the β- and γ-isomerides were found to be identical, whilst that of the α-ester was entirely different. When solutions of the α-ester were kept under observation, however, the change from enol- to keto-form could be clearly followed, until, after three weeks, the absorption curve coincided with those of the keto-esters. The method was therefore invaluable as a means of distinguishing between stereoisomeric and structurally isomeric bodies.

A paper of classical interest is that on the constitution of cotarnine by Dobbie, Lauder, and Tinkler, in the *Journal* of 1903. Cotarnine, a colourless base, becomes highly coloured in alcoholic solution, but not in ether or chloroform. Hydrocotarnine and cyanohydrocotarnine remain colourless in all these solvents. The latter two exhibit similar spectra to cotarnine in ether or chloroform, whilst cotarnine hydrochloride is coloured and its absorption curve conforms to that of contarnine in water or alcohol. By purely chemical methods it was impossible to ascribe satisfactory structural formulæ to these nearly related compounds, but by the spectroscopic method it was decided that cotarnine, as suggested by Decker, is the carbinol base (A) which changes to the ammonium base (B) in alcohol or in acid solution. On the other hand, alkali reverses the change to the

carbinol structure, and the striking series of absorption spectra photographs accompanying this work enables one clearly to visualise the gradual transition which occurs in contact with these various

(A) $C_8H_6O_3<\begin{matrix}CH(OH)\cdot NMe\\ CH_2\text{——}CH_2\end{matrix}$ $C_8H_6O_3<\begin{matrix}CH{=}NMe\cdot OH\\ CH_2\text{–}CH_2\end{matrix}$ (B)

reagents. A similar result was obtained in the case of hydrastinine, and the same method applied also to phenylmethylacridol. Absorption spectra data gave valuable information as to the structural and stereochemical relationships of many of the alkaloids, including papaverine, laudanine, hydrastine, narcotine, gnoscopine, narceine, laudanosine, quinidine, and cinchonine. An independent examination of more than thirty alkaloids was made by Dobbie and his collaborators in the course of their work.

In 1903 he was offered and accepted the post of Director of the Royal Scottish Museum, Edinburgh, but he relinquished his professorship with regret and even with misgivings. The new appointment was, however, under the Scottish Education Department and, in accepting it, he had reasons for anticipating that he would have some share in shaping educational policy in Scotland and be able to continue his researches. These expectations he was able to fulfil only in part, although he continued his investigations on alkaloids and absorption spectra under increasing difficulties.

His wide interests, versatility, and scholarship, combined with his administrative ability, made him an excellent Director. With characteristic energy and judgment, he threw himself into the work of the Museum and increased its popularity and usefulness. He greatly extended the collection of Egyptian antiquities, a subject in which he was much interested, expanded the section devoted to engineering and engineering models, and collected a large fund by public subscription in order to acquire for the Museum the valuable Noel Paton collection of Scottish armour and weapons.

In 1909 he was appointed by the Treasury as Principal of the Government Laboratory in succession to Sir Edward Thorpe. At the time, the laboratory was in the throes of reorganisation. The junior staff was technically under the control of the Board of Customs and Excise, but in 1911 the whole became a separate State Department under the Treasury, and Dobbie received the title of Government Chemist. To this department were referred all chemical questions arising from other branches of the State, and a perusal of the annual reports reveals the perplexing variety of problems which were investigated from time to time alongside the routine examinations of food, drugs, and excisable articles. The subjects ranged, for example, from investigations into the pigments,

paper, and gum to be used in the new issue of postage stamps to a detailed report on the condition and methods of preservation of the roof timbers of Westminster Hall. In January, 1915, the King bestowed on him the honour of knighthood.

The years 1914—1919 brought grim pressure to bear on the work of the Government Laboratory and the reports for these years are in themselves an epitome of the war in all its phases. Immediately on the outbreak of war the Government Chemist set in motion on his own initiative a vast reorganisation of the laboratory in order to cope with the analysis of food and of all contractors' stores sent out for the Army and Navy. The bewildering complexity of the problem did not disturb the orderly and systematic direction of the Department, which, under its chief, carried on its work silently, but with such effect that none of the consumable stores sent overseas provided occasion for complaint as to their wholesomeness.

His services were sought by the Treasury on multifarious Committees called into being during these years of national peril, such as the Research Committee of the War Cabinet and the Nitrogen Products Committee, and following the armistice he was a member of the Royal Commission for Awards to Inventors and of the University Grants Committee. For fourteen years he also served as scientific adviser for the research endowment scheme of the Carnegie Trust for the Universities of Scotland.

Sir James Dobbie had passed the normal age for retirement before the cessation of hostilities and carried on at the wish of his superiors. But in April 1918 his elder son died from wounds received in action in France, and this grief, together with the strain of overwork, began to tell on his health, which doubtless received permanent injury.

In 1919, Sir James was elected President of the Chemical Society, an honour which he greatly valued. He had warmly appreciated the invitation to serve as a member of Council in 1901—1906, and as a Vice-President in 1907—1911. He also took pride in his Presidency of the Institute of Chemistry during 1915—1917. Both at the Institute and at the Chemical Society his term of office was marked by changes in the constitution which were especially appreciated by their younger members. No one who attended the informal meetings of the Chemical Society held during his presidency will readily forget the way in which he sought out the younger men, interested himself in their scientific activities, and gave friendly encouragement.

He was elected a Fellow of the Royal Society in 1904 and received the honorary degree of LL.D. from Glasgow in 1908, and that of D.Sc. from Wales in 1920.

During the earlier post-war years he resumed his researches on absorption spectra and published with J. J. Fox three papers in the *Proceedings of the Royal Society* bearing on a new aspect of the subject. The study of the molecular constitution of sulphur, selenium, and tellurium in the state of vapour revealed what seemed to be the existence of molecules of $S_3$, on the analogy of ozone. Similar phenomena were shown also with selenium and tellurium. The transition from the molecules $S_2$ and $S_8$ appeared to be well marked and corresponded also with measurements of density. The character of the absorption of light by the halogen elements at elevated temperatures possesses unusual features pointing to a similar tendency towards polymerisation.

Sir James Dobbie retired from the Government Laboratory in 1920 and went to reside permanently at his house at Fairlie, Ayrshire, which hitherto had served for him and his family as a summer retreat. He filled his leisure with reading in the ample library he had collected, and regained freshness and vigour amid surroundings which he greatly loved. After a visit to Italy with Lady Dobbie in the spring of 1924 he died of heart failure following a short illness; he was laid to rest in the Largs cemetery on the slope of the hill overlooking the sea and within view of the village of Fairlie.

Dobbie had attainments other than those which were apparent from his scientific and administrative work. He was a man of scholarly and artistic tastes, deeply versed in general literature and archæology, and a good classic. Those who were privileged to see this more intimate side will always remember him as the most modest, kindly and courteous of men, a wise counsellor, a delightful conversationalist and companion. He was beloved by his students and fellow-workers, and in the lives of all his friends he leaves a blank which can never be filled.

W. N. H.
A. L.

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## OTTO HEHNER.

BORN 1853; DIED SEPTEMBER 9TH, 1924.

OTTO HEHNER, who died on September 9th, 1924, in his seventieth year, had been a fellow of the Society since 1876, and served on the Council from 1895 to 1899. He was born in 1853 at Marienberg (Nassau), and received his chemical training at Wiesbaden, where his father held a high judicial office. He was a pupil and subsequently assistant in the laboratory of Fresenius, and was later assistant to Neubauer. In 1873, he migrated to Glasgow to become assistant to Gustav Bischof in the then Andersonian College, where

he had as a colleague the late Sir William Ramsay, with whom he retained a close friendship until the time of Ramsay's death. From Glasgow he came south to Ventnor as assistant to the late Dr. A. H. Hassall, well remembered for his pioneer work in the detection of food adulterants, carried out under commission from the *Lancet*. Hassall, although a fine microscopist, was, perhaps, not very strong as a chemist, and he was glad of the co-operation of Hehner as that of an ardent young chemist well trained in analytical methods. It was here that Hehner quite suddenly established an early reputation by devising, in collaboration with his fellow assistant, Angell, the first rational method of making anything like an approximate quantitative differentiation between butter-fat and the other fats with which it was then liable to be adulterated, based upon the proportion of fatty acids insoluble in water. The "Hehner Value" of fats is still determined and recorded as a matter of routine in the examination of any new oil or fat. Various other workers pursued the subject by devising methods of directly determining what may be called the "reciprocal value," *viz.*, that of the fatty acids soluble in water. Among these were Dupré and Muter, also ardent pioneers among the little band of food analysts who were brought into official existence by the Sale of Food and Drugs Act. Later, Reichert followed with his empirical distillation of the volatile fatty acids, the examination of which was subsequently further refined by Polensky, Kirschner, and others. But it was Hehner's work which gave the original impulse to all that followed.

In 1877, Hassall removed his laboratory to London, and Hehner was taken into partnership, and from the death of Hassall onwards Hehner continued to practise his profession in London.

His initial work on butter-fat was but the forerunner of extensive detailed research on the chemistry of fats, and incidentally it may be mentioned that he was the first to establish the constitution of beeswax. At the beginning of his career the whole subject of food analysis was in a primitive and chaotic condition compared with the position it occupies to-day. The Sale of Food and Drugs Act and the difficulties of making it effective necessarily called for a concentration of effort on the subject, and among those who responded to it Hehner was not only one of the most industrious, but also one of the most able. He had shrewd and rapid insight and foresight, and he was an omnivorous reader and the happy possessor of an abnormally retentive memory.

It is not necessary to recapitulate the titles of his long list of public papers on food analysis and cognate subjects; reference to the earlier volumes of the *Analyst* will show that there was scarcely a topic connected with the chemistry of food and sanitation to the

advancement of which his personal researches did not make some valuable contribution, while, at the same time, there was scarcely any branch of chemistry, whether theoretical or applied, with which he did not possess an acquaintance that was more than superficial. While, therefore, in the narrower capacity of public analyst, he early became recognised as perhaps the leading authority on what was always his favourite subject, he also gradually came to be regarded as a wise and safe consultant in multifarious other branches of applied chemistry, and over many years it was rarely that any considerable problem of chemical litigation was thrashed out without his assistance, particularly in the intricate field of patent disputation. He was equally at home in questions relating to the industrial production of organic dyestuffs and in those relating to the chemistry of what used to be regarded as the "rare earths" until the development of incandescent lighting brought them into commercial importance.

The writer of this notice had the happiness of making Hehner's acquaintance even before he settled in London, and of enjoying his intimate friendship down to the time of his death. After the original honorary secretaries (and virtual founders) of the Society of Public Analysts, Heisch and Wigner, were successively promoted to its presidency, Hehner and the writer took their places as honorary secretaries of the Society, and in this capacity were colleagues for eleven years, until, in 1891, Hehner was elected president. In this close companionship, the writer probably had greater opportunities than many other of his numerous friends of appreciating and profiting by his extraordinarily encyclopædic knowledge, and of esteeming the sterling worth of his really lovable character.

Hehner was a past Vice-President of the Institute of Chemistry and took an active part in its work from nearly the time of its foundation.

His loyalty to the country of his adoption was as the loyalty of one British-born. During the war he placed at the disposal of the Government the very special knowledge and experience which he had acquired as the recognised principal expert in glycerine, and he went far towards wearing himself out in the (strictly honorary) work which he did for the Ministry of Munitions in this direction.

It was fortunate that his career was not cut short during the war by an incident of the first daylight air raid over London, during which a bomb crashed through the roof of his laboratory in Billiter Square, penetrating successively the various floors of the building and burying itself in the basement, fortunately without exploding,

although in its descent it decapitated one of the occupants of the building.

Although the late Lord Moulton placed on record his appreciation of Hehner's valuable work for the country during the war, there were, no doubt, delicate reasons which would have made a full public recognition of his services difficult at the time; and when the war at last was over, there were, unhappily, among the local authorities whom he served as public analyst, and even among his clients, some who, knowing nothing of his loyal services and little of the man himself, did not seek to conceal that they had no exemption for him in the attitude which they too sweepingly assumed towards those of our fellow subjects who were of German birth. Among his fellow chemists and others who really knew him, there was never any shadow of such feeling; but his sensitive nature, nevertheless, suffered, and after a time he went to seek rest and change on a long visit to the Transvaal, where his son is engaged in farming. This was in 1921. Although he believed that he would be there hidden in rural obscurity, his presence was soon detected by the South African Government, who promptly enlisted his consultative services for the time being.

The sudden death of his partner, the late R. G. Grimwood, at the end of 1922 caused him to return to England, where, for a time, he resumed active work; but having found a new partner in Dr. H. E. Cox, he embarked on a second visit to South Africa, where, shortly before the time he had fixed for his permanent return, he was seized with some form of tropical fever, from the effect of which, after an apparent recovery, he died suddenly.

BERNARD DYER.

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## EDMUND KNOWLES MUSPRATT.

BORN 1833; DIED SEPTEMBER 1ST, 1923.

IN the University Club in Liverpool there is a portrait of E. K. Muspratt painted by Augustus John. The portrait depicts him in the robes of an honorary Doctor of Laws of the University he loved and for which he had laboured long and strenuously. The portrait was presented to Dr. Muspratt when the University conferred upon him the honorary degree in 1907. It is fitting that this portrait should hang where it does, for of all the activities and achievements of a long life devoted to public service, that with which Edmund Knowles Muspratt would wish his memory to be particularly associated would be the birth and troubled infancy of the University of Liverpool. In writing of him as a man of science, as a great

industrialist, and as a politician, it is well to remember that over and above all he was a seer and a prophet in the cause of education.

Dr. Muspratt was born into an age of great political development and achievement. Indeed, in looking back over his long life, it is impossible not to marvel at the vast changes in the civilised world.

I may quote from the admirable and sympathetic memoir written by Mr. T. P. O'Connor, M.P. :

"Just realise that this man knew Munich when Lola Montez could topple over a throne; that he travelled in Italy when there were passports and Custom houses between a dozen different principalities; when the Austrians still ruled over Lombardy and Venice; that he travelled through many parts of Europe and through a great part of Ireland by stage coach instead of by railway; that he heard the fall of Sebastopol announced in the theatre at Keswick; that he lived in the house in which he died when it was practically in the country, with a little rivulet at the end, where William Ewart Gladstone gathered primroses as a boy and where railway sidings and warehouses now stand; that he heard Richard Cobden make a speech in favour of international arbitration at a meeting in Frankfort-on-the-Main; that he saw, as a beautiful girl of twelve, Helen Donniges, the woman whose love brought Lassalle, the first great German Socialist leader, to death in a duel; that he knew and partly assisted Cyrus Field in his many attempts, until final success, to connect London and America by cable; that he heard Rachel in Paris; and was the godson of Sheridan Knowles, the once-famous dramatist; that he lived in intimate association with Liebig, the greatest of German chemists; and saw administered to his sick sister for the first time a famous decoction for feeding and soothing a diseased digestion; that as a youth he saw the first great Exhibition in London, and then the first Exposition at Paris in the palmiest days of Louis Napoleon; that he was a youth and even already actively interested in politics before Disraeli became a Minister for the first time, and that he took a part in negotiating the French Commercial Treaty with Cobden in 1862."

Muspratt was the son of a remarkable father, James Muspratt, a man who, in his long life, had been a soldier, sailor, chemist, a pioneer of scientific industry, a giant of the industrial revolution, and withal a man of culture, wide interests, and public spirit. From his earliest years his son Edmund was accustomed to meet at his father's house the most eminent literary, scientific, and artistic people of the time. James Muspratt's was a vivid personality, and to him his son owed much.

When he was ten years of age Edmund was sent to Dr. Heldenmaier's school at Worksop, where the teaching, based on the principles of Pestalozzi, was very different from that of the ordinary English school of that day. It was then thoroughly unorthodox. There was a chemical laboratory in the school, besides a natural history museum, and the teaching of science and modern languages was based on the then unprecedented method of reasoning and practice. At sixteen, young Muspratt was sent to Giessen University to study under Liebig, his father's great friend. This relationship with Liebig was perhaps the most vitalising influence of his life. Liebig became his hero, and while Liebig was alive they were the warmest friends.

James Muspratt, wise in his generation, saw to it, however, that his son should have the opportunity of developing wide interests, and in his earliest years he introduced his son to all that was best in the drama and literature of the day. Later, he encouraged him to extensive travel in Europe and America, so that by the time he was twenty-one years of age, E. K. Muspratt was singularly well equipped for a young Englishman of that time.

The time had then arrived for a definite choice of career to be made. In a letter to his sister at that time he tells how his original intention of studying medicine had given way to more particular scientific studies. He considers other professions, and he says of politics "Politics, in spite of myself, absorb all my thoughts." However, the decision was quickly made for him. His father had built chemical works at Widnes, Flint, and Liverpool. At these works the Leblanc process for the manufacture of soda ash was in operation. His father needed assistance in the conduct of his business, and thus E. K. Muspratt commenced his association with the chemical industry—an association that closed only with his death.

The value of the scientific training he had received was soon apparent. The period of wasteful manufacture was now over and a new era of technical efficiency in chemical industry was opening. To the many problems facing the industry, young Muspratt applied all that intellectual keenness and restless energy which characterised him throughout life, and by the utilisation of fresh sources of raw material, the working up of by-products, and the recovery of waste, he succeeded in maintaining the supremacy of the family business. An example of his method may be quoted. Having introduced Spanish pyrites into this country as a source of sulphur for sulphuric acid, he determined to master the problem of the extraction of copper from the burnt ore. He therefore set out to study metallurgy. While still controlling the works at Liverpool and Widnes

he arranged to take a course of practical study at Owens College in Manchester, but even there he found no satisfactory facilities, and worked more or less independently in a cellar in the College. He soon ceased to attend Owens, but continued his independent work, with the result that in a short time he started a new works in Widnes, of which he was chairman, for the extraction of copper and silver from the burnt ore of Spanish pyrites.

No new process was suggested or adopted in any part of the world which he did not investigate and if satisfied did not immediately instal for the better conduct of his business. He induced his father to make extensive and expensive alterations and additions to his works, with the result that there was built up one of the largest and most successful alkali businesses in the world.

Muspratt was perhaps the first manufacturer of standing to attach sufficient importance to the research side of industry. It was natural, considering his own training, that he should look upon Germany as the then source of supply of research chemists, but he had a sure faith in the ultimate success of research schools in this country, and the Muspratt Laboratory at Liverpool University is the monument of that faith which was gloriously justified in his time.

When the United Alkali Company was formed in 1890 the Muspratt firm was perhaps the most important constituent firm, and Dr. Muspratt became Chairman of the General Management Committee of the new company. Though a dominating influence on the commercial side of the industry, yet his keenest interest was always reserved for the technical and scientific side. His first act under the new *régime* was the establishment of a central research laboratory, carefully planned and fully staffed by able chemists.

Almost ten years before, he had been instrumental in founding the Society of Chemical Industry. In 1881, a few alkali manufacturers of Widnes and St. Helens met Dr. Campbell Brown (later the first Professor of Chemistry at Liverpool University) in the room of the Royal Infirmary School of Medicine to discuss the possibility of closer co-operation and more intimate contact between professional scientists and manufacturers and technical chemists. They approached Professor Henry Roscoe of Owens College, Manchester, who cordially supported the idea of the new Society, and the Society of Chemical Industry was launched. The first President was Roscoe himself, who presided at the first annual meeting in London in 1881. At this meeting Dr. Muspratt read a paper on noxious gases legislation, and the amending Act which was shortly after passed in Parliament was based on the principles laid down in this

paper. A few years later, Dr. Muspratt became president, and at his death he was the senior vice-president of the society.

Great as were his services to chemical industry, his services to education in connection with the establishment of Liverpool University, and particularly to the cause of scientific education in this country were still greater. On the occasion of his eightieth birthday an address was presented to him by the professors of the University, in which grateful recognition is given to his "skill, tenacity, and courage in opposing, with or without hope, all narrow and destructive policy, by whomsoever urged." It proceeds—"No one here, therefore, has promoted the cause of learning and academic statesmanship longer, more wisely, or with a more single mind." The signatories to this remarkable document include Professors Mackay, Elton, Henry Cecil Wylde, E. C. C. Baly, and Sir Charles Sherrington. Professor F. G. Donnan, who had been the first occupant of the Muspratt Chair of Physical Chemistry, wrote at the same time: "What you did for Chemical Science at Liverpool University the world already knows. And the splendid laboratory which you built, equipped and endowed there will continue for generations to advance the cause of chemical science, and, may I add, to add lustre to the honourable name which it bears."

The establishment of civic universities in England will be regarded as one of the great landmarks of the Victorian era, and in the dramatic and often heart-breaking struggles of that time, Dr. Muspratt played a leading part.

But throughout all his busy life he never deserted his first love for politics. In his youth a political career was impracticable, but his early interest in the great political questions of the time continued. With every phase of the growth of individual liberty Dr. Muspratt was in sympathy. His main political work was in the domain of public finance. He was the moving spirit of the Financial Reform Association, which had for its aims "public economy, just taxation, and perfect freedom of trade." He was an individualist who believed that the cause of the State was best served by the freedom of the individual to work out his salvation in his own way. Freedom of thought, freedom of action, freedom of trade, were to him the very principles of his being.

Muspratt took a leading part in the municipal politics of Liverpool, particularly in connexion with the adoption of the Vyrnwy water scheme, and with the advancement of technical education. Only once did he contest a Parliamentary election. This was at Widnes, when he did not succeed. It is well, perhaps, that he did not. The public work which he accomplished in Liverpool and south-west Lancashire was probably of infinitely greater value to

the community than any services he might have rendered at Westminster.

To those who knew him and were in intimate contact with him, Dr. Muspratt will live as a vivid memory. Although determined in policy and unsparing in debate, he was always kind and approachable. Muspratt did not suffer fools gladly and humbug and pretence called forth his bitter scorn, but there are many of a younger generation in scientific industry who gratefully recall his helpful advice and kindly interest. His was essentially a young mind and even during the last few years of his life, darkened as they were by blindness, he never failed in zest and sympathy, and the youthful alertness of his mind and the trenchant forcefulness of his conversation were a delight and an inspiration to his friends. The indomitable courage of the man shone out in his attitude towards the blindness which overtook him. No murmurings or vain regrets ever left his lips. His interest in the daily affairs of life was not lessened one whit. He engaged a staff of readers by whom all the latest scientific and political literature was read to him and by whose means he was kept informed of the daily happenings reported in the Press.

The reaction against the Victorian age has now died out and we recall with pride its story of development and achievement. Dr. Muspratt was a product of that age, and the story of his life, full and many-sided, devoted to great causes and abiding principles, is the story of one who played an honourable and a strenuous part in a great formative period of British history.

G. C. CLAYTON.

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**Uric acid**, solvent action of trimethylenetriamines on, and its trimethyl- and triethyl- trimethylenetriamine salts (GRAYMORE), 2284.

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**Viscosity**, determination of transition points from (HARTSHORNE), 2096.

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**Water**, effect of salts on the vapour pressure of (SIDGWICK and EWBANK), 2273.
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**Tap-water**, hard, volumetric estimation of carbonic acid in (CROWTHER and MARTIN), 1937.
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*o*-**Xylene**, 4-chloro-3:5-*di*hydroxy-, and its dibenzoyl derivative (HINKEL), 1851.
**Xylenes**, extraction of, from crude xylol (PATTERSON, MCMILLAN, and SOMERVILLE), 2488.
**Xylenes**, ω-bromo-, isomeric, polarity effects in (SHOESMITH and SLATER), 2278.
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*o*-**Xylenols**, 5:6-*di*chloro-, and their benzoyl derivatives (HINKEL), 1851.
**Xylol**, extraction of xylenes from (PATTERSON, MCMILLAN, and SOMERVILLE), 2488.
**Xylose**, preparation of, from esparto cellulose (IRVINE and HIRST), 24.
**1:8-Xyloylnaphthalenecarboxylic acids** (MASON), 2122.

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**Zinc**, hydrogen overvoltage of (WESTRIP), 1112.
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**Zinc alloys**, with aluminium and cadmium (BUDGEN), 1642.
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**Zirconium** *tetra*chloride, anhydrous, preparation of (MORGAN and BOWEN), 1255.
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# FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus $C_1$ group, $C_2$ group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

## $C_1$ Group.


**CHN** Hydrocyanic acid, production of, from explosion of nitrogen and acetylene (GARNER and SAUNDERS), 1634; potassium salt, double salts of, with copper, gold, silver, and thallium cyanides (BASSETT and CORBET), 1660.

**$CHCl_3$** Chloroform, action of potassium phenoxide on (BAINES and DRIVER), 907.

**$CH_2O_2$** Formic acid, properties of mixtures of aniline, water, and (POUND and RUSSELL), 769.

**$CH_4O$** Methyl alcohol, action of hydrogen chloride on (CARTER and BUTLER), 963.

**$CSCl_2$** Thiocarbonyl chloride, reactions of (DYSON and GEORGE), 1702.

1 III

**$CHO_6N_3$** *aci*-Nitroform, potassium salt, alkaline reduction of (GRIFFITHS and HUNTER), 463.

**$CH_3ON$** Formamide, cryoscopic constant of (LOWRY and CUTTER), 1469.

1 IV

**$CHO_4N_2Cl$** Chlorodinitromethane, and its salts (GOTTS and HUNTER), 446.

**$CH_4O_2NS$** Methanesulphonamide, reactions of diazo-salts with (DUTT), 1463.

**$CH_6NCl_4I$** Methylammonium tetrachloroiodide (CHATTAWAY and GARTON), 187.

**$CH_6N_3Cl_4I$** Guanidine tetrachloroiodide (CHATTAWAY and GARTON), 185.

**$CO_4N_2ClI$** Chloroiododinitromethane (GOTTS and HUNTER), 448.

1 V

**$CH_7O_2N_2Cl_4I$** Carbamide tetrachloroiodide (CHATTAWAY and GARTON), 185.


## $C_2$ Group.


**$C_2H_2$** Acetylene, tautomerism of, and its halogen derivatives (INGOLD), 1528; explosion of mixtures of nitrogen and (GARNER and SAUNDERS), 1634; condensation of, with hydrogen sulphide in presence of catalysts (TOMKINSON), 2264.

**$C_2H_4$** Ethylene, spontaneous combustion of, during preparation of ethylene dichloride (SHARMA), 2676.

### 2 II

$C_2H_4O_2$ Acetic acid, purification of (Orton and Bradfield), 960 ; properties of mixtures of aniline, water, and (Pound and Russell), 769 ; electrical conductivity of mixtures of aniline, water, and (Pound), 1560 ; equilibria of, with homologues of aniline (O'Connor), 1422.

$C_2H_4Br_2$ Ethylene bromide, decomposition of, by potassium and sodium iodide solutions (Patterson and Robertson), 1526.

$C_2H_6O$ Ethyl alcohol, adiabatic cooling of (Pushin and Grebenshchikov), 2045 ; solubility of substances in mixtures of water and (Wright), 2068 ; chlorination of (Chattaway and Backeberg), 1097 ; reaction of phenylmethylcarbamyl chloride with (Price), 115.

### 2 III

$C_2HClI_2$ Di-iodo*iso*acetylene (Ingold), 1535.

$C_2H_2N_4S_2$ Dithio-*p*-urazine disulphide (Guha and De), 1217.

$C_2H_4N_4S_2$ Dithio-*p*-urazine, and its silver salt (Guha and De), 1217.

$C_2O_8N_2K_2$ *s*-Dipotassium tetranitroethane, halogenation of (Hunter), 1480.

$C_2O_8N_4Cl_2$ *s*-Dichlorotetranitroethane (Hunter), 1482.

### 2 IV

$C_2H_4ON_4S$ Monothio-*p*-urazine (Guha and De), 1217.

$C_2H_8NCl_4I$ Dimethylammonium tetrachloroiodide (Chattaway and Garton), 187.

Ethylammonium tetrachloroiodide (Chattaway and Garton), 188.

### 2 V

$C_2H_{14}O_2N_2Cl_8I_2$ Ethylenediammonium bistetrachloroiodide (Chattaway and Garton), 188.

## $C_3$ Group.

$C_3H_4O_3$ Ethylene carbonate, preparation of (Allpress and Maw), 2261.

Pyruvic acid, tautomerism of phenylhydrazones of (Stevens and Ward), 1324.

$C_3H_4O_4$ Malonic acid, action of bromine on, in aqueous solution (West), 1277.

$C_3H_4O_6$ Mesoxalic acid, tautomerism of phenylhydrazones of (Stevens and Ward), 1324.

$C_3H_5I$ Allyl iodide, action of potassium pentasulphide on (Thomas and Riding), 2214.

$C_3H_6O$ Acetone, density and viscosity of, at low temperatures (Archibald and Ure), 726.

$C_3H_8O_3$ Glycerol, adiabatic cooling of (Pushin and Grebenshchikov), 2045 ; mutual solubility of, and amino- and hydroxy-compounds (Parvatiker and McEwen), 1484 ; estimation of, by a modified dichromate method (Bennett), 1971.

### 3 III

$C_3H_5O_4N$ Nitroquinol, dissociation constant of (Prideaux and Nunn), 2110.

$C_3H_6N_4S$ Dimethylenethiocarbohydrazide (Guha and De), 1216.

$C_3H_7O_2N$ Urethane, adiabatic cooling of, and its mixtures with benzene (Pushin and Grebenshchikov), 2045.

### 3 IV

$C_3H_3O_5N_3S$ 4(or 5)-Nitroglyoxaline-5(or -4)-sulphonic acid (Balaban and Pyman), 1571.

$C_3H_{10}NCl_4I$ Trimethylammonium tetrachloroiodide (Chattaway and Garton), 188.

### 3 V

$C_3H_5ONClBr$ Chlorobromoacetomethylamide, crystallography of (Knaggs), 1442.

$C_3H_5ONClI$ Chloroiodoacetomethylamide (McKie), 1076.

## $C_4$ Group.

$C_4H_6O_6$ Tartaric acid, anomalous rotatory dispersion in (Lowry and Cutter), 1465; potassium antimony salt, structure of (Wark), 2007.

*r*-Tartaric acid, resolution of (Wren and Hughes), 1739.

$C_4H_{10}N_2$ Piperazine, hydroferricyanide of (Cumming), 2542.

### 4 III

$C_4HO_2Cl_3$ Chlorofumaryl chloride, action of, on aromatic amines and hydrazines (Chattaway and Parkes), 464.

$C_4H_4O_5Cu$ Cuprimalic acid, constitution of, and its salts (Wark), 2004.

$C_4H_4N_2Br_2$ 4:5-Dibromo-1-methylglyoxaline, and its salts (Balaban and Pyman), 1564.

$C_4H_5O_2N_3$ 4- and 5-Nitro-1-methylglyoxalines, and their salts (Hazeldine, Pyman, and Winchester), 1434.

$C_4H_5N_2Cl$ 5-Chloro-1-methylglyoxaline, and its nitrate (Balaban and Pyman), 1572.

$C_4H_5N_2Br$ Bromo-1-methylglyoxalines, and their salts (Balaban and Pyman), 1568.

$C_4H_6ON_2$ Methylpyruvonitrile oxime, and its silver salt (Walker), 1625.

### 4 IV

$C_4H_4O_2N_3Cl$ 5-Chloro-4-nitro-1-methylglyoxaline (Balaban and Pyman), 1572.

$C_4H_4O_2N_3Br$ Bromonitromethylglyoxalines (Balaban and Pyman), 1569.

$C_4H_5O_2N_2Cl$ Chlorofumarodiamide (Chattaway and Parkes), 467.

$C_4H_5O_5N_3S$ 4-Nitro-1-methylglyoxaline-5-sulphonic acid, and its sodium salt (Balaban and Pyman), 1569.

$C_4H_6O_3N_2S$ 2-Methylglyoxaline-4-sulphonic acid, and its salts (Forsyth, Moore, and Pyman) 921.

$C_4H_6O_6N_2S_2$ 2-Methylglyoxaline-4:5-disulphonic acid, and its salts (Forsyth, Moore, and Pyman), 922.

$C_4H_7ONCl_2$ Dichloroacetoethylamide, crystallography of (Knaggs), 1442.

$C_4H_7O_2N_2Br$ Bromomethylmalonamide (Stevens and Ward), 1329.

$C_4H_{10}NCl_4I$ Diethylammonium tetrachloroiodide (Chattaway and Garton), 188.

$C_4H_{12}N_2Cl_8I_2$ Piperazine bistetrachloroiodide (Chattaway and Garton), 187.

### 4 V

$C_4H_5O_3N_2BrS$ Bromo-1-methylglyoxalinesulphonic acids (Balaban and Pyman), 1568.

$C_4H_7ONClBr$ Chlorobromoacetoethylamide, crystallography of (Knaggs), 1442.

$C_4H_7ONClI$ Chloroiodoacetoethylamide (McKie), 1076.

## $C_5$ Group.

$C_5H_5N$ Pyridine, hydroferricyanide of (Cumming), 2542.

$C_5H_6O_6$ Methylene tartaric acid, and its barium salt, and their rotation (Austin and Campbell), 1943.

$C_5H_{10}O_2$ *n*-Butyric acid, properties of mixtures of aniline, water, and (Pound and Russell), 769.

$C_5H_{11}N$ Piperidine, hydroferricyanide of (Cumming), 2542; additive compounds of, with diallyl and dibenzyl pentasulphides (Thomas and Riding), 2217.

### 5 III

$C_5H_4O_3N_4$ Uric acid, triethyl- and trimethyl-trimethylenetriamine salts (Graymore), 2284.

$C_5H_9NBr_2$ Dibromopiperidine, additive compound of, with diallyl pentasulphide dibromide (Thomas and Riding), 2216.

### 5 IV

$C_5H_6NCl_4I$ Pyridinium tetrachloroiodide (CHATTAWAY and GARTON), 186.
$C_5H_7ON_2Br$ 5-Bromo-2-hydroxymethyl-1-methylglyoxaline, and its picrate (BALABAN and PYMAN), 1569.
$C_5H_7O_2F_2B$ Boron acetylacetone difluoride (MORGAN and TUNSTALL), 1964.
$C_5H_8O_2N_2Te$ *cyclo*Telluropentane-3:5-dionedioxime (MORGAN and DREW), 1605.
$C_5H_8O_2N_2I$ 4(or 5)-Nitro-1:3-dimethylglyoxalinium iodide (HAZELDINE, PYMAN, and WINCHESTER), 1436.
$C_5H_8N_2BrI$ 4(or 5)-Bromo-1:3-dimethylglyoxalinium iodide (BALABAN and PYMAN), 1570.
$C_5H_9O_2N_2Br$ Bromoethylmalonamide (STEVENS and WARD), 1329.
$C_5H_{10}O_3N_4S$ Diacetylthiocarbohydrazide (GUHA and DE), 1216.

### 5 V

$C_5H_{14}ONCl_4I$ Piperidinium tetrachloroiodide (CHATTAWAY and GARTON), 187.

## $C_6$ Group

$C_6H_6$ Benzene, adiabatic cooling of, and its mixtures with urethane (PUSHIN and GREBENSHCHIKOV), 2045; effect of intensive drying on (SMITS), 1071; reactions of thiocarbamides with chloronitro-derivatives of (TAYLOR and DIXON), 243.

### 6 II

$C_6H_6O$ Phenol, adiabatic cooling of, and its mixtures with *p*-toluidine (PUSHIN and GREBENSHCHIKOV), 2044; nitration of (ARNALL), 811.
$C_6H_6O_2$ *allo*Maltol (YABUTA), 578.
$C_6H_6O_6$ Dimethylene tartrate, and its rotation (AUSTIN and CARPENTER), 1943.
$C_6H_7N$ Aniline, properties of mixtures of water, fatty acids, and (POUND and RUSSELL), 769; electrical conductivity of mixtures of acetic acid, water, and (POUND), 1560; direct sulphonation of (HODGSON), 1855; hydroferricyanide of (CUMMING), 2542.
$C_6H_8O_4$ *trans-cyclo*Butane-1:2-dicarboxylic acid, resolution of, and its *l*-quinine salt (GOLDSWORTHY), 2012.
$C_6H_8O_6$ Carbomethoxyglycerol carbonate (ALLPRESS and MAW), 2262.
$C_6H_8N_2$ *as*-Dimethylsuccinonitrile (DICKENS, HORTON, and THORPE), 1838.
Phenylenediamines, hydroferricyanides of (CUMMING), 2542.
Phenylhydrazine, reaction of glucose with (KNECHT and THOMPSON), 222; estimation of, volumetrically (KNECHT), 1544.
$C_6H_{10}O_3$ Ethyl acetoacetate, interaction of *o*-hydroxydistyryl ketones with (FORSTER and HEILBRON), 340; (HEILBRON and FORSTER), 2064.
$C_6H_{10}O_4$ Adipic acid, thallous salt (MENZIES and WILKINS), 1150.
$C_6H_{10}O_6$ Dicarbomethoxyglycol (ALLPRESS and MAW), 2261.
*r*-Dimethoxysuccinic acid (WREN and HUGHES), 1742.
$C_6H_{10}S_2$ Diallyl disulphide, and its silver nitrate and mercuric chloride compounds (THOMAS and RIDING), 2466.
$C_6H_{10}S_5$ Diallyl pentasulphide, and its additive compound with piperidine (THOMAS and RIDING), 2216.
$C_6H_{12}O_6$ Dextrose, reaction of phenylhydrazine with (KNECHT and THOMPSON), 222; estimation of (KNECHT and HIBBERT), 2009.
α-Glucose, mutarotation of (BAKER, INGOLD, and THORPE), 290.
Lævulose, estimation of (KNECHT and HIBBERT), 2011.
$C_6H_{12}N_4$ Hexamethylenetetramine, hydroferricyanide of (CUMMING), 2542.
$C_6H_{14}O_6$ Mannitol, condensation of olive oil with (IRVINE and GILCHRIST), 10.
$C_6H_{15}N_3$ Trimethyltrimethylenetriamine, and its salts (GRAYMORE), 2284.

## 6 III

$C_6H_3O_7N_3$ Picric acid, chromammine salts of (KING), 1332.

$C_6H_3N_2Cl_3$ Dichlorophenylazoimides (CHATTAWAY, GARTON, and PARKES), 1988.

$C_6H_3N_6Co$ Hydrocobalticyanic acid, potassium salt, hydrolysis of, by sulphuric acid (BASSETT and CORBET), 1358.

$C_6H_3N_6Fe$ Hydroferricyanic acid, salts of, with organic bases (CUMMING), 1106, 2541; potassium salt, hydrolysis of, by sulphuric acid (BASSETT and CORBET), 1358.

$C_6H_4O_4N_2$ *m*-Dinitrobenzene, influence of pressure on the freezing point of (PUSHIN), 2628; sulphonation of (GRIFFITHS), 1401.

$C_6H_4O_6N_2$ Dinitroquinol, dissociation constant of (PRIDEAUX and NUNN), 2110.

$C_6H_4N_6Fe$ Hydroferrocyanic acid, salts of, with organic bases (CUMMING), 1106, 2541.

$C_6H_5OK$ Potassium phenoxide, action of chloroform on (BAINES and DRIVER), 907.

$C_6H_5O_2N$ Nitrobenzene, cryoscopy with (BROWN and BURY), 2219; (SIDGWICK and EWBANK), 2268.

$C_6H_5O_3Cl$ 5-Hydroxy-2-chloromethyl-γ-pyrone (YABUTA), 578.

$C_6H_5O_3Br$ 5-Hydroxy-2-bromomethyl-γ-pyrone (YABUTA), 579.

$C_6H_5O_3I$ 5-Hydroxy-2-iodomethyl-γ-pyrone (YABUTA), 580.

$C_6H_5O_5N_3$ Picramic acid, chromammine salt of (KING), 1335.

$C_6H_5N_2Cl$ Benzenediazonium chloride, reaction of methanesulphonamide with (DUTT), 1464.

$C_6H_7O_2N$ 4:5-Dihydroxy-2-methylpyridine (YABUTA), 584.

$C_6H_8O_4Br_2$ αβ-Dibromo-β-methylglutaconic acid (INGOLD, OLIVER, and THORPE), 2134.

αβ-Dibromo-α-(or -γ-)methylglutaric acid (INGOLD, OLIVER, and THORPE), 2134.

Methyl dibromosuccinates (ING and PERKIN), 1822.

$C_6H_8Br_2S_5$ Diallyl pentasulphide dibromide, additive compounds of, with dibromopiperidine (THOMAS and RIDING), 2216.

$C_6H_8Br_2S_5$ Diallyl pentasulphide tribromide (THOMAS and RIDING), 2216.

$C_6H_{10}I_4S_5$ Diallyl pentasulphide tetraiodide (THOMAS and RIDING), 2216.

$C_6H_{12}O_2N_2$ *as*-Dimethylsuccinamide (DICKENS, HORTON, and THORPE), 1839.

Methylmalondimethylamide (WEST), 717.

$C_6H_{15}N_2Br_2$ Trimethyltrimethylenetriamine dibromide (GRAYMORE), 2284.

## 6 IV

$C_6H_2O_4N_2Cl_2$ 1:3-Dichlorodinitrobenzene (SANÉ and JOSHI), 2483.

$C_6H_2O_4N_2Cl$ 2:4-Dinitrochlorobenzene, action of, on aldoximes (BRADY and TRUSZKOWSKI), 1087.

$C_6H_3O_5N_2Cl$ 3-Chlorodinitrophenol (SANÉ and JOSHI), 2483.

$C_6H_2N_2Cl_6I$ Dichlorobenzenediazonium tetrachloroiodides (CHATTAWAY, GARTON, and PARKES), 1983.

$C_6H_4O_2Cl_2S$ 2:5-Dichlorobenzenesulphinic acid (SMILES and GIBSON), 179.

$C_6H_4N_2Cl_5I$ Chlorobenzenediazonium tetrachloroiodides (CHATTAWAY, GARTON, and PARKES), 1983.

$C_6H_5N_2Cl_4I$ Benzenediazonium tetrachloroiodide (CHATTAWAY, GARTON, and PARKES), 1982.

$C_6H_8NCl_4I$ α-Picolinium tetrachloroiodide (CHATTAWAY and GARTON), 186.

$C_6H_9O_2N_2Cl$ Chlorofumarodimethylamide (CHATTAWAY and PARKES), 467.

$C_6H_{10}O_2N_2Br_2$ αα′-Dibromoadipamide (BERNTON, ING, and PERKIN), 1502.

$C_6H_{10}O_2N_2I_2$ αα′-Di-iodoadipamide (BERNTON, ING, and PERKIN), 1502.

$C_6H_{11}O_2N_2Br$ α-Bromo-α′-methylmalondimethylamide (WEST), 718.

$C_6H_{14}O_5NCl$ Glucosamine, estimation of (KNECHT and HIBBERT), 2011.

## 6 V

$C_6H_2O_4N_2ClBr$ 1-Chloro-2-bromo-4:6-dinitrobenzene (SANÉ and JOSHI), 2482.

$C_6H_2N_2Cl_4Br_2I$ 2:4:6-Tribromobenzenediazonium tetrachloroiodide (CHATTAWAY, GARTON, and PARKES), 1983.

$C_6H_3N_2Cl_4Br_2I$ 2:4-Dibromobenzenediazonium tetrachloroiodide (CHATTAWAY, GARTON, and PARKES), 1983.

$C_6H_4O_2N_2Cl_4I$ Nitrobenzenediazonium tetrachloroiodides (CHATTAWAY, GARTON, and PARKES), 1983.

# $C_7$ Group.

$C_7H_6O_2$ Salicylaldehyde, thallous salt (MENZIES and WILKINS), 1149.

$C_7H_6O_3$ Salicylic acid, disalicylatodiethylenediamminocobaltic salt (MORGAN and SMITH), 2004.

$C_7H_8O_5$ Comenic acid methyl ether (YABUTA), 581.

$C_7H_6O_8$ *cyclo*Propane-1:2:2:3-tetracarboxylic acids (ING and PERKIN), 1824.

$C_7H_7Cl$ Benzyl chloride, reaction of water and (HARKER), 500.

*p*-Chlorotoluene, photochemical action of iodine on moist (SILBERRAD), 2196; nitration of (HODGSON and ANDERSON), 2195.

$C_7H_8O_2$ Guaiacol, influence of pressure on the freezing point of (PUSHIN), 2628.

$C_7H_8O_3$ *allo*Maltol methyl ether (YABUTA), 579.

$C_7H_9N$ Benzylamine, hydroferricyanide of (CUMMING), 2542.

Methylaniline, hydroferri- and hydroferro-cyanides of (CUMMING), 2541.

*p*-Toluidine, adiabatic cooling of, and its mixtures with phenol (PUSHIN and GREBENSHCHIKOV), 2045.

Toluidines, equilibria of acetic acid with (O'CONNOR), 1422; hydroferricyanides of (CUMMING), 2542.

$C_7H_{10}O_3$ Allyl carbonate (FIERZ-DAVID and MÜLLER), 26.

$C_7H_{10}O_6$ Carbethoxyglycerol carbonate (ALLPRESS and MAW), 2263.

$C_7H_{12}O_4$ Pimelic acid, thallous salts (MENZIES and WILKINS), 1150.

$C_7H_{14}O_5$ Methyl mannitan (IRVINE and GILCHRIST), 14.

$C_7H_{14}O_6$ γ-Methylmannoside (IRVINE and BURT), 1345.

## 7 III

$C_7H_4NCl$ *p*-Chlorophenylcarbylamine (INGOLD), 97.

$C_7H_4NBr$ *p*-Bromophenylcarbylamine (INGOLD), 98.

$C_7H_5O_3N$ *o*-Nitrobenzaldehyde, photochemical transformation of (BOWEN, HARTLEY, SCOTT, and WATTS), 1218.

$C_7H_5O_4Cl$ Comenyl chloride methyl ether, and its hydrochloride (YABUTA), 582.

$C_7H_5O_6N_3$ *as*-Trinitrotoluenes, reactions of (BRADY, HEWETSON, and KLEIN), 2400.

$C_7H_6OBr_2$ Dibromo-*p*-cresol (GRIFFITH), 2626.

$C_7H_6O_2Cl_2$ 3:5-Dichloro-2:6-dimethylpyrone (MORGAN and PORTER), 1276.

$C_7H_6NCl$ Methylene-*p*-chloroaniline (INGOLD), 93.

$C_7H_6NBr$ Methylene-*p*-bromoaniline (INGOLD), 93.

$C_7H_7ON_2$ *p*-Nitrotoluene, effect of pressure on the freezing point of (PUSHIN), 2628.

$C_7H_7O_2Cl$ 3-Chloro-5-acetyl-4-hydroxy-2-methylfuran (MORGAN and PORTER), 1276.

5-Methoxy-2-chloromethyl-γ-pyrone (YABUTA), 578.

$C_7H_7O_3Cl_3$ Trichlorodiacetylacetone (MORGAN and PORTER), 1277.

$C_7H_7O_3I$ 5-Methoxy-2-iodomethyl-γ-pyrone (YABUTA), 581.

$C_7H_7O_4N$ Comenamic acid methyl ether, and its salts (YABUTA), 583.

Comenamide methyl ether (YABUTA), 582.

$C_7H_7N_2Cl$ *p*-Toluenediazonium chloride, reaction of methanesulphonamide (DUTT), 1464.

$C_7H_8O_3N_2$ α-Cyano-ββ-dimethylsuccinimide (DICKENS, HORTON, and THORPE), 1838.

$C_7H_8O_4S$ *m*-Cresolsulphonic acids, salts of (HAWORTH, LAPWORTH, and WILSON), 1304.

$C_7H_9O_3As$ *o*-Tolylarsinic acid (BURTON and GIBSON), 2276.

$C_7H_9O_4Br$ α-Bromo-αβ(or -βγ)-dimethylglutaconic acid (INGOLD, OLIVER, and THORPE), 2135.

$C_7H_9NO$ *o*-Anisidine, hydroferricyanide of (CUMMING), 2542.

$C_7H_9N_2Cl$ 6-Chloro-2:5-tolylenediamine (MORGAN and GLOVER), 1600.

$C_7H_{10}ON_4$ δ-Anilinosemicarbazide, and its hydrochloride (SUTHERLAND and WILSON), 2146.

$C_7H_{10}O_2Te$ Tellurium *n*-butyryl acetone (MORGAN, DREW, and PORTER), 737.

Tellurium dipropionylmethane (MORGAN, DREW, and ACKERMAN), 741.

Tellurium 3-methylpropionylacetone (MORGAN and DREW), 746.

*cyclo*Tellurodimethylpentane-3:5-diones (MORGAN and DREW), 1605.

$C_7H_{10}O_3N_2$ β-Carbamyl-α-cyano-ββ-dimethylpropionic acid (DICKENS, HORTON, and THORPE), 1838.

$C_7H_{10}O_4Br_2$ αβ-Dibromo-αγ-dimethylglutaric acid (INGOLD, OLIVER, and THORPE), 2135.

$C_7H_{13}O_2N_3$ Piperidino-oxalylhydrazine, and its hydrochloride (WILSON and PICKERING), 1155.

$C_7H_{14}O_2N_2$ Ethylmalondimethylamide (WEST), 718.

## 7 IV

$C_7H_3O_4NBr_2$ 2:4-Dibromo-6-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1054.

$C_7H_3O_4NI_2$ Di-iodonitrohydroxybenzaldehydes (HENRY and SHARP), 1055.

$C_7H_3O_5NBr_2$ Dibromonitrohydroxybenzoic acids (HENRY and SHARP), 1054.

$C_7H_3O_5NI_2$ Di-iodo-4-nitro-3-hydroxybenzoic acid (HENRY and SHARP), 1057.

$C_7H_3O_5NHg_2$ 2:3-Anhydro-2:6-dihydroxydimercuri-4-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1056.

$C_7H_3NCl_2S$ 2:4-Dichlorophenylthiocarbimide (CHATTAWAY, HARDY, and WATTS), 1554.

$C_7H_3NBr_2S$ 2:4-Dibromophenylthiocarbimide (CHATTAWAY, HARDY, and WATTS), 1554.

$C_7H_4O_2ClAs$ *o*-Carboxyphenylchloroarsinous anhydride (AESCHLIMANN and MCCLELAND), 2030.

$C_7H_4O_4NI$ Iodonitrohydroxybenzaldehydes (HENRY and SHARP), 1053.

$C_7H_4NBrS$ *p*-Bromophenyl thiocyanate (CHALLENGER and COLLINS), 1379.

$C_7H_5O_2NCl_2$ 4-Chloro-5-methoxypyridine-2-carboxylic acid chloride (YABUTA), 583.

$C_7H_5O_3NI_2$ Di-iodo-4-nitro-*m*-cresol (HENRY and SHARP), 1057.

$C_7H_5O_3N_2Cl$ 2-Chloro-6-nitroso-3-nitrotoluene (MORGAN and GLOVER), 1600.

$C_7H_5O_4N_2Cl$ *o*-Chlorodinitrotoluenes (MORGAN and GLOVER), 1597.

$C_7H_5O_5NHg$ 5-Hydroxymercuri-3-nitro-4-hydroxybenzaldehyde (HENRY and SHARP), 1052.

$C_7H_5O_6N_5S$ Picryl-*S*-thiocarbamide, and its salts (TAYLOR and DIXON), 248.

$C_7H_6ONCl$ Formo-*p*-chloroanilide, silver salt of (FARROW and INGOLD), 2552.

$C_7H_6O_3NBr$ *o*-Nitrobenzyl bromide (SHOESMITH, HETHERINGTON, and SLATER), 1316.

$C_7H_6O_3NCl$ 4-Chloro-5-methoxypyridine-2-carboxylic acid (YABUTA), 584.

$C_7H_6O_3NBr$ Bromonitrocresol (GRIFFITH), 2628.

3-Nitro-4-hydroxybenzyl bromide (SHOESMITH, HETHERINGTON, and SLATER), 1317.

$C_7H_6O_7N_2S$ Dinitrotoluenesulphonic acids, sodium salts (BRADY, HEWETSON, and KLEIN), 2402.

$C_7H_6N_2Cl_2S$ 2:4-Dichlorophenylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1554.

$C_7H_6N_2Br_2S$ 2:4-Dibromophenylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1555.

$C_7H_7O_3N_2Cl$ 6-Chloro-5-nitro-*o*-toluidine (MORGAN and GLOVER), 1599.

$C_7H_7O_2ClS$ *p*-Toluenesulphonyl chloride, action of, on nitrophenols (SANÉ and JOSHI), 2481.

$C_7H_7O_6NS$ Nitrocresolsulphonic acid, potassium salts (GRIFFITH), 2627.

$C_7H_7N_3Cl_4I$ Toluenediazonium tetrachloroiodides (CHATTAWAY, GARTON, and PARKES), 1983.

$C_7H_{10}O_3Cl_2Te$ *cyclo*Telluri-4:4-dimethylpentane-3:5-dione 1:1-dichloride (MORGAN and DREW), 1604.

Tellurium *n*-butyrylacetone dichloride (MORGAN, DREW, and PORTER), 737.

Tellurium dipropionylmethane dichloride (MORGAN, DREW, and ACKERMAN), 740.

Tellurium 3-methylpropionylacetone dichloride (MORGAN and DREW), 746.

$C_7H_{10}NCl_4I$ Benzylammonium tetrachloroiodide (CHATTAWAY and GARTON), 188.

$C_7H_{11}O_3NTe$ *cyclo*Tellurodimethylpentane-3:5-dione monoximes (MORGAN and DREW), 1606.

$C_7H_{12}O_2N_2Te$ *cyclo*Tellurodimethylpentane-3:5-dione dioximes (MORGAN and DREW), 1606.

*cyclo*Telluroethylpentane-3:5-dione dioximes (MORGAN and DREW), 1605.

$C_7H_{13}O_2N_2Br$ α-Bromo-α′-ethylmalondimethylamide (WEST), 719.

### 7 V

$C_7H_3O_2N_2BrS$ 4-Bromo-2-nitrophenyl thiocyanate (CHALLENGER and COLLINS), 1379.

$C_7H_3O_4NCl_2Hg_2$ Dichlorodimercurinitrohydroxybenzaldehydes (HENRY and SHARP), 1054.

$C_7H_4O_4NClHg$ Chloromercurinitrohydroxybenzaldehydes (HENRY and SHARP), 1052.

$C_7H_7O_2NCl_2S$ *p*-Toluenesulphondichloroamide, hydrolysis of, in water (SOPER), 1899.

$C_7H_7O_4N_4ClS$ Substance, and its picrate, from 1-chloro-2:4-dinitrobenzene and thiocarbamide (TAYLOR and DIXON), 247.

$C_7H_8O_3NCl_4I$ Pyridine-betaine tetrachloroiodide (CHATTAWAY and GARTON), 187.

## $C_8$ Group.

$C_8H_{10}$ Xylenes, extraction of, from crude xylol (PATTERSON, MCMILLAN, and SOMERVILLE), 2488.

### 8 II

$C_8H_6O_3$ Piperonal, absorption spectra of (PURVIS), 410.

$C_8H_6O_4$ Piperonylic acid, absorption spectra of (PURVIS), 410.

$C_8H_8O_3$ Piperonyl alcohol, absorption spectra of (PURVIS), 410.

$C_8H_{10}O$ *m*-4-Xylenol, absorption spectra of (PURVIS), 406.

$C_8H_{10}O_4$ 5-Ethoxy-2-hydroxymethyl-γ-pyrone (YABUTA), 580.

$C_8H_{12}O_6$ *cyclo*Pentane-1:2:3-tricarboxylic acid, potassium salt (BERNTON, ING, and PERKIN), 1498.

$C_8H_{11}N$ Dimethylaniline, equilibrium of acetic acid with (O'Connor), 1426; hydroferri- and hydroferro-cyanides of (Cumming), 2541.

$C_8H_{14}O_3$ 3-Ethylpropionylacetone, and its copper salt (Morgan and Thomason), 757.

3-*n*-Propylacetylacetone, and its copper salt (Morgan and Thomason), 758.

*n*-Valerylacetone, and its copper salt (Morgan and Holmes), 761.

$C_8H_{14}O_3$ Hexahydromandelic acid, synthesis and resolution of (Wood and Comley), 2636.

$C_8H_{14}O_4$ $\alpha\alpha$-Diethylsuccinic acid (Dutt and Thorpe), 2528.

$C_8H_{14}O_6$ Dicarbethoxyglycol (Allpress and Maw), 2262.

Ethyl tartrate, molecular weight of (Lowry and Cutter), 1465.

$C_8H_{16}O_6$ Methyl methylglucoside (Irvine and Gilchrist), 9.

$C_8H_{16}O_3$ $\beta\gamma$-Dihydroxybutyric acid, barium salt (Ingold, Oliver, and Thorpe), 2135.

$C_8H_{18}O$ *sec.*-Octyl alcohol, rotatory power of (Lowry and Richards), 1595.

## 8 III

$C_8H_5O_2N$ Isatin, estimation of, volumetrically (Knecht), 1544.

$C_8H_5N_3Br_2$ 1-(2:4-Dibromophenyl)-1:2:3-triazole (Chattaway, Garton, and Parkes), 1988.

$C_8H_5N_3Cl_2$ 1-Dichlorophenyl-1:2:3-triazoles (Chattaway, Garton, and Parkes), 1988.

$C_8H_6OBr_2$ $\omega$-Bromo-*p*-toluoyl bromide (Shoesmith, Hetherington, and Slater), 1314.

$C_8H_7O_2As$ *o*-Carboxyphenylmethylarsinous anhydride (Aeschlimann and McCleland), 2033.

$C_8H_7O_3N$ Isatic acid, thallous salt (Menzies and Wilkins), 1149.

$C_8H_7O_3Br_3$ 1:2:3-Tribromo-5-hydroxy-4:6-dimethoxybenzene, and its sodium salt (Alimchandani), 543.

$C_8H_8OCl_2$ Dichloro-*o*-xylenols (Hinkel), 1851.

$C_8H_8OCl_4$ 2:4:5:6-Tetrachloro-1:1-dimethyl*cyclo*-$\Delta^4$-hexen-3-one (Hinkel), 1854.

$C_8H_8O_6S$ 3-Methoxysulphobenzoic acids, hydrogen potassium salts (Haworth, Lapworth, and Wilson), 1306.

$C_8H_9OCl_3$ 3:4:5-Trichloro-1:1-dimethyl-$\Delta^4$-*cyclo*hexen-3-one (Hinkel), 1850.

$C_8H_9O_2Cl$ 4-Chloro-3:5-dihydroxy-*o*-xylene (Hinkel), 1851.

$C_8H_9O_4N$ 5-Methoxy-1-methyl-4-pyridone-2-carboxylic acid (Yabuta), 586.

$C_8H_9O_4As$ *o*-Carboxyphenylmethylarsinic acid (Aeschlimann and McCleland), 2034.

$C_8H_{10}ON_2$ *p*-Nitrosodimethylaniline, hydroferri- and hydroferro-cyanides of (Cumming), 2541.

$C_8H_{10}O_3Cl$ 4:5-Dichloro-1:1-dimethyl-$\Delta^5$-*cyclo*hexen-3-one (Hinkel), 1852.

$C_8H_{10}O_6S$ 4-Hydroxy-3:5-dimethoxybenzenesulphonic acid ($+1\frac{1}{2}H_2O$) and its salts (Alimchandani), 542.

$C_8H_{10}NBr$ *p*-Bromodimethylaniline, hydroferri- and hydroferro-cyanides of (Cumming), 2541.

$C_8H_{11}O_2N$ 5-Methoxy-1:2-dimethyl-4-pyridone (Yabuta), 584.

$C_8H_{11}O_3N$ 5-Ethoxy-2-hydroxymethyl-4-pyridone, and its picrate (Yabuta), 580.

$C_8H_{12}O_3Te$ Tellurium 3-ethylpropionylacetone (Morgan and Thomason), 757.

Tellurium propionyl-*n*-butyrylmethane (Morgan, Drew, and Ackerman), 742.

Tellurium 3-*n*- and *iso*-propylacetylacetones (Morgan and Thomason), 758.

Tellurium *n*-valerylacetone (Morgan and Holmes), 761.

$C_8H_{12}O_4Br_2$ Ethyl *dl*-dibromosuccinate (Ing and Perkin), 1822.

Methyl dibromoadipate (Bernton, Ing, and Perkin), 1500.

$C_8H_{12}O_4I_2$ Methyl di-iodoadipates (BERNTON, ING, and PERKIN), 1501.
$C_8H_{12}O_3N_2$ *cyclo*Pentane-1:2:3-tricarboxylamide (BERNTON, ING, and PERKIN), 1497.
$C_8H_{15}O_2N$ Hexahydromandelamide (WOOD and COMLEY), 2637.
$C_8H_{16}O_2N_2$ *n*- and *iso*-Propylmalondimethylamides (WEST), 718.

## 8 IV

$C_8H_5O_5N_3Cl_2$ *N*:6-Dichloro-2:4-dinitroacetanilide (CHATTAWAY and DOWDEN), 1196.
$C_8H_5O_6NHg$ Formoxymercuri-4-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1056.
$C_8H_5O_7N_4Cl$ *N*-Chloro-2:4:6-trinitroacetanilide (CHATTAWAY and DOWDEN), 1196.
$C_8H_6ONBr$ 3-Bromo-*p*-methoxybenzonitrile (BRADY and MANJUNATH), 1064.
$C_8H_6O_2N_2S$ 2-Nitro-*p*-tolyl thiocyanate (CHALLENGER and COLLINS), 1379.
$C_8H_6O_5N_3Cl$ *N*-Chloro-2:4-dinitroacetanilide (CHATTAWAY and DOWDEN), 1196.
$C_8H_7O_3NCl$ Methyl 4-chloro-5-methoxypyridine-2-carboxylate (YABUTA), 584.
$C_8H_7O_4NS$ Methoxy-*o*-benzoicsulphinides (HAWORTH and LAPWORTH), 1306.
$C_8H_8ONCl$ Acetochloroanilides, freezing-point curves for mixtures of (ORTON and OWEN), 766.
Phenylmethylcarbamyl chloride, reaction of ethyl alcohol with (PRICE), 115.
$C_8H_8ONBr$ *p*-Bromoacetanilide, nitration of (GRIFFITH), 940.
$C_8H_8O_2NBr$ 3-Bromo-*p*-methoxybenzaldoximes (BRADY and MANJUNATH), 1064.
$C_8H_8O_2ClAs$ *o*-Carboxyphenylmethylchloroarsine (AESCHLIMANN and MCCLELAND), 2034.
$C_8H_8O_3NBr$ 3-Nitro-4-methoxybenzyl bromide (SHOESMITH, HETHERINGTON, and SLATER), 1317.
$C_8H_9O_4N_3Br$ 2-Bromo-4:6-dinitrodimethylaniline (SANÉ and JOSHI), 2483.
$C_8H_9O_3NS$ Acetanilide-*p*-sulphinic acid (BERE and SMILES), 2361.
$C_8H_9O_5NS$ 3-Methoxy-4-sulphonamidobenzoic acid (HAWORTH and LAPWORTH), 1306.
$C_8H_{12}O_2Cl_2Te$ Tellurium 3-ethylpropionylacetone dichloride (MORGAN and THOMASON), 757.
Tellurium propionyl-*n*-butyrylmethane dichloride (MORGAN, DREW, and ACKERMAN), 742.
Tellurium 3-*n*- and -*iso*-propylacetylacetone dichlorides (MORGAN and THOMASON), 758.
Tellurium *n*-valerylacetone dichloride (MORGAN and HOLMES), 761.
$C_8H_{13}NCl_4I$ Collidinium tetrachloroiodide (CHATTAWAY and GARTON), 186.
$C_8H_{13}O_3Cl_3Te$ Tellurium ethyl *O*-ethyl acetoacetate trichloride (MORGAN and DREW), 753.
$C_8H_{15}O_2N_2Br$ α-Bromo-α′-*n*- and -*iso*-propylmalondimethylamides (WEST), 719.

## 8 V

$C_8H_7ONCl_2S$ Methyl 2:4-dichlorophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1554.
$C_8H_{13}O_2N_4Cl_4I$ Caffeine tetrachloroiodide (CHATTAWAY and GARTON), 187.

# $C_9$ Group.

$C_9H_6N_2$ 6-Cyanindole (KERMACK), 2290.
$C_9H_7N$ Quinolines, hydroferricyanides of (CUMMING), 2542.
$C_9H_8N_2$ 2-Aminoquinoline (HAMER), 1353.
$C_9H_{10}O_2$ *o*- and *p*-Tolyl acetates, action of sodium on (HALL), 2266.
$C_9H_{10}O_3$ Dihydrocoumaric acid, β-sulphonates of (DEY and ROW), 557.
β-Hydroxy-β-phenylpropionic acid, conversion of, into β-bromo-β-phenylpropionic acids (SENTER and WARD), 2137.

$C_9H_{12}N_2$ 1-Cyano*cyclo*hexane-1-acetonitrile (DICKENS, HORTON, and THORPE), 1834.

$C_9H_{13}N$ Mesidine, equilibrium of acetic acid with (O'CONNOR), 1426.

$C_9H_{14}O_4$ Ethyl ethylidenemalonate, action of anilinophenylacetonitrile with (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2339.

$C_9H_{14}O_5$ Ethyl acetonedicarboxylate, thallous ester (MENZIES and WILKINS), 1151.

$C_9H_{14}O_9$ Tricarbomethoxyglycerol (ALLPRESS and MAW), 2263.

$C_9H_{16}O_2$ 3-*n*-Butylacetylacetone, and its copper salt (MORGAN and HOLMES), 763.
Dibutyrylmethane and its copper salt (MORGAN and THOMASON), 756.
Dipropionylethylmethane, and its copper salt (MORGAN and DREW), 748.
*n*-Hexoylacetone, and its copper salt (MORGAN and HOLMES), 762.

$C_9H_{16}O_5$ Dimethyl anhydro-methylglucoside (IRVINE and GILCHRIST), 9.

$C_9H_{16}O_7$ Dicarbethoxyglycerol (ALLPRESS and MAW), 2263.

$C_9H_{18}O_5$ Trimethyl mannitan (IRVINE and GILCHRIST), 15.

$C_9H_{20}O$ *d*-γ-Nonanol, rotatory power of ethers of (KENYON and BARNES), 1395.

$C_9H_{21}N_3$ Triethyltrimethylenetriamine, and its salts (GRAYMORE), 2284.

## 9 III

$C_9H_4O_2Cl_2$ 6:8-Dichlorocoumarin (DEY and ROW), 560.

$C_9H_5O_2I$ 6-Iodocoumarin (DEY and ROW), 560.

$C_9H_6O_3Cl_2$ 3:5-Dichlorocoumaric acid (DEY and ROW), 562.

$C_9H_6O_3Br_2$ 3:5-Dibromocoumaric acid (DEY and ROW), 562.

$C_9H_7O_2N$ Indole-6-carboxylic acid (KERMACK), 2291.

$C_9H_7O_2N_3$ 2-Nitrophenylglyoxalines, and their salts (PYMAN and STANLEY), 2485.

$C_9H_7O_3Cl$ 5-Chlorocoumaric acid (DEY and ROW), 562.

$C_9H_7O_3Br$ 5-Bromocoumaric acid (DEY and ROW), 562.

$C_9H_7O_5N$ 5-Nitrocoumaric acid, and its silver salt (DEY and ROW), 563.

$C_9H_7O_6N$ 2-Methylpyridine-3:4:6-tricarboxylic acid, and its salts (LAWSON, PERKIN, and ROBINSON), 633.

$C_9H_7N_3Cl_2$ 1-Dichlorophenyl-5-methyl-1:2:3-triazoles (CHATTAWAY, GARTON, and PARKES), 1991.

$C_9H_8ON$ Phenylpyruvonitrile oxime, and its silver salt (WALKER), 1625.

$C_9H_8O_2N$ *p*-Tolyloxamonitrile (PLOWMAN and WHITELEY), 599.

$C_9H_8O_2N_2$ Nitroso-4-tetrahydroquinolone (CLEMO and PERKIN), 1619.

$C_9H_8O_3N_2$ Nitrocinnam*syn*aldoximes (BRADY and GRAYSON), 1420.
Nitro-5-methoxyindoles (BLAIKIE and PERKIN), 323.

$C_9H_8O_3Br_2$ 3:5-Dibromodihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 559.

$C_9H_8O_7N_2$ 3:5-Dinitrodihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 559.

$C_9H_8NBr$ α-Bromo-β-phenylpropionitrile (BAKER and LAPWORTH), 2337.

$C_9H_9ON$ Methoxyindoles (BLAIKIE and PERKIN), 296.
4-Tetrahydroquinolone, synthesis of (CLEMO and PERKIN), 1608.

$C_9H_9O_3I$ 5-Iododihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 559.

$C_9H_9O_5N$ 5-Nitrodihydrocoumaric acid, β-sulphonates of (DEY and ROW), 557.
Nitro-2:3-dimethoxybenzaldehydes (PERKIN, ROBINSON, and STOYLE), 2355.
2-Nitromethoxyphenylacetic acids (BLAIKIE and PERKIN), 308.

$C_9H_{10}O_3Cl_2$ 3:5-Dichlorodihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 558.

$C_9H_{10}O_4N_2$ 3-Nitro-*p*-methoxybenzaldoxime methyl ethers (BRADY and MANJUNATH), 1062.

$C_9H_{10}O_5N_2$ 5-Nitro-3:4-dimethoxybenz*anti*aldoxime (BRADY and MANJUNATH), 1067.
$C_9H_{11}ON$ 4-Hydroxytetrahydroquinoline (CLEMO and PERKIN), 1621.
Nitrosomesitylene, preparation of (INGOLD and PIGGOTT), 173.
$C_9H_{12}O_2N_2$ Nitrosomethyl-*p*-phenetidine (STEDMAN), 1375.
$C_9H_{12}O_6S$ 3:4:5-Trimethoxybenzenesulphonic acid ($+1\frac{1}{2}H_2O$) and its salts (ALIMCHANDANI), 541.
$C_9H_{13}O_3N$ 1-Carboxy*cyclo*hexane-1-acetimide (DICKENS, HORTON, and THORPE), 1836.
$C_9H_{13}NBr_2$ *p*-Bromophenyltrimethylammonium bromide (READE), 151.
$C_9H_{13}NBr_4$ *p*-Bromophenyltrimethylammonium perbromide (READE), 150.
$C_9H_{14}O_2Te$ Tellurium 3-*n*-butylacetylacetone (MORGAN and HOLMES), 763.
Tellurium dibutyrylmethane (MORGAN and THOMASON), 757.
Tellurium 3:3-diethylacetylacetone (MORGAN and DREW), 750.
Tellurium dipropionylethylmethane (MORGAN and DREW), 749.
Tellurium 3-ethyl-*n*-butyrylacetone (MORGAN and DREW), 748.
Tellurium *n*-hexoylacetone (MORGAN and HOLMES), 762.
$C_9H_{15}ON$ ψ-Pelletierine, synthesis of (MENZIES and ROBINSON), 2163.
$C_9H_{15}O_3N$ *cyclo*Hexylmalonamic acid (ROBINSON), 228.
$C_9H_{16}O_2N_2$ 1-Carbamyl*cyclo*hexane-1-acetamide (DICKENS, HORTON, and THORPE), 1837.
Nitrosotriacetonamine, influence of colloids on the decomposition of (FINDLAY and THOMAS), 1244.
$C_9H_{18}O_2N_2$ *n*- and *iso*-Butylmalondimethylamides (WEST), 719.

## 9 IV

$C_9H_4O_4NBr$ 8-Bromo-6-nitrocoumarin (DEY and ROW), 560.
$C_9H_4O_4NI$ 8-Iodo-6-nitrocoumarin (DEY and ROW), 561.
$C_9H_5O_8NHg_2$ 2:6-Diformoxydimercuri-4-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1056.
$C_9H_6O_2NBr$ 8-Bromo-6-aminocoumarin (DEY and ROW), 561.
$C_9H_6O_2NI$ 8-Iodo-6-aminocoumarin (DEY and ROW), 561.
$C_9H_6O_5NBr$ 3-Bromo-5-nitrocoumaric acid (DEY and ROW), 563.
$C_9H_7O_6NHg$ Acetoxymercurinitrohydroxybenzaldehydes (HENRY and SHARP), 1052, 1059.
$C_9H_7O_7NHg_2$ Hydroxymercuriacetoxymercurinitro-3-hydroxybenzaldehydes (HENRY and SHARP), 1055.
$C_9H_7NCl_5I$ Chloroquinolinium tetrachloroiodides (CHATTAWAY and GARTON), 186.
$C_9H_8O_5NBr$ 3-Bromo-5-nitrodihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 559.
$C_9H_8O_5NI$ 3-Iodo-5-nitrodihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 559.
$C_9H_8NCl_4I$ Quinolinium tetrachloroiodide (CHATTAWAY and GARTON), 186.
$C_9H_9ONCl_2$ Dichloroacetomethylanilide, crystallography of (KNAGGS), 1443.
$C_9H_9O_3NCl$ Ethyl 4-chloro-5-methoxypyridine-2-carboxylate (YABUTA), 584.
$C_9H_9O_3N_2Cl$ *N*-Chloronitroaceto-*p*-toluidides (CHATTAWAY and DOWDEN), 1197.
$C_9H_{10}ONBr$ α-Bromo-β-phenylpropionamide (BAKER and LAPWORTH), 2338.
$C_9H_{10}O_2NBr$ 3-Bromo-*p*-methoxybenzaldoxime methyl ethers (BRADY and MANJUNATH), 1065.
$C_9H_{12}NClBr$ *p*-Bromophenyltrimethylammonium chloride (READE), 154.
$C_9H_{12}NCl_2Br_2$ *p*-Bromophenyltrimethylammonium bromide dichloride (READE), 156.

$C_9H_{13}NBrI_3$ *p*-Bromophenyltrimethylammonium tri-iodide (READE), 152.
$C_9H_{13}NBr_2I_2$ *p*-Bromophenyltrimethylammonium bromide di-iodide (READE), 155.
$C_9H_{13}NBr_3I$ *p*-Bromophenyltrimethylammonium bromide iodobromide (READE), 154.
$C_9H_{14}O_2Cl_2Te$ Tellurium 3-*n*-butylacetylacetone dichloride (MORGAN and HOLMES), 763.
Tellurium dibutyrylmethane dichloride (MORGAN and THOMASON), 757.
Tellurium diethylacetylacetone dichloride (MORGAN and DREW), 750.
Tellurium dipropionylethylmethane dichloride (MORGAN and DREW), 748.
Tellurium 3-ethyl-*n*-butyrylacetone dichloride (MORGAN and DREW), 747.
Tellurium *n*-hexoylacetone dichloride (MORGAN and HOLMES), 762.
$C_9H_{15}O_2Cl_3Te$ Tellurium dibutyrylmethane trichloride (MORGAN and THOMASON), 757.
Tellurium *O*-ethyl-*n*-butyrylacetone trichloride (MORGAN, DREW, and PORTER), 738.
Tellurium *O*-ethyl*iso*butyrylacetone trichloride (MORGAN and DREW), 743.
Tellurium *O*-ethylpropionylmethane trichloride (MORGAN, DREW, and ACKERMAN), 741.
$C_9H_{17}O_2N_2Br$ α-Bromo-α′-*n*-*iso*-butylmalondimethylamides (WEST), 719.

9 V

$C_9H_7O_2N_2Cl_4I$ 6-Nitroquinolinium tetrachloroiodide (CHATTAWAY and GARTON), 186.
$C_9H_9ONClI$ Chloroiodoacetobenzylamide (McKIE), 1076.
Chloroiodoacetomethylanilide (McKIE), 1076.
$C_9H_9ONCl_2S$ Ethyl 2:4-dichlorophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1554.
$C_9H_9ONBr_2S$ Ethyl 2:4-dibromophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1555.
$C_9H_{13}NClBr_2I$ *p*-Bromophenyltrimethylammonium bromide iodochloride (READE), 155.
$C_9H_{13}NCl_2BrI$ *p*-Bromophenyltrimethylammonium chloride iodochloride (READE), 153.
$C_9H_{13}NCl_4BrI$ *p*-Bromophenyltrimethylammonium chloride iodotrichloride (READE), 152.

## $C_{10}$ Group.

$C_{10}H_{16}$ β-Pinene, oxidation of (HENDERSON and CHISHOLM), 107.
Sabinene, oxidation of, with chromyl chloride (HENDERSON and ROBERTSON), 765.

10 II

$C_{10}H_8O_3$ 1-Ketohydrindene-3-carboxylic acid (SPEIGHT, STEVENSON, and THORPE), 2190.
$C_{10}H_8O_4$ 3:7-Dihydroxy-2-methylchromone (ALLAN and ROBINSON), 2193.
$C_{10}H_9N$ β-Naphthylamine, hydroferricyanide of (CUMMING), 2542.
$C_{10}H_{10}O_2$ 2-Hydroxystyryl methyl ketone, isomerism of (McGOOKIN and HEILBRON), 2099.
$C_{10}H_{10}O_3$ *p*-Anisyl β-hydroxyvinyl ketone (PRATT, ROBINSON, and WILLIAMS), 202.
4-Carboxy-2:6-dimethylbenzaldehyde (PERKIN and TAPLEY), 2435.
4-Methyl-*o*-coumaric acid, silver salt (DEY and ROW), 562.
$C_{10}H_{10}O_{10}$ Carbomethoxyfructose dicarbonate (ALLPRESS and HAWORTH), 1228.
$C_{10}H_{10}N_2$ 4- and 5-Phenyl-1-methylglyoxalines, and their salts (HAZELDINE, PYMAN, and WINCHESTER), 1436.

$C_{10}H_{11}O_2$ *n*- and *iso*-Eugenols, absorption spectra of (PURVIS), 408.
$C_{10}H_{12}N_2$ 3-Hydrazinoquinaldine (G. M. and R. ROBINSON), 833.
$C_{10}H_{12}O_2$ Eugenol, ultra-violet absorption spectrum of (THOMPSON), 962.
$C_{10}H_{12}O_5$ 4-Methyldihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 557.
$C_{10}H_{12}N_4$ 5-Amino-4-*p*-aminophenyl-1-methylglyoxaline, dihydrochloride of (HAZELDINE, PYMAN, and WINCHESTER), 1440.
$C_{10}H_{14}O$ Carvacrol, absorption spectra of (PURVIS), 406.
Thymol, absorption spectra of (PURVIS), 406.
$C_{10}H_{14}O_2$ Camphorquinone, absorption spectra of (LOWRY and FRENCH), 1921; rotatory dispersion of (LOWRY and RICHARDS), 2511.
$C_{10}H_{14}N_2$ 1-Cyano*cyclo*heptane-1-acetonitrile (DICKENS, HORTON, and THORPE), 1840.
$C_{10}H_{16}O$ Camphor, absorption spectra of (LOWRY and FRENCH), 1921.
Citral, absorption spectra of (PURVIS), 416.
Piperitone (READ, SMITH, and HUGHESDON), 129.
Pulegone, absorption spectra of (PURVIS), 414.
$C_{10}H_{16}O_3$ α-Hydroxycampholenic acid (BURGESS), 2378.
$C_{10}H_{16}O_4$ 1-Carboxy*cyclo*heptane-1-acetic acid (DICKENS, HORTON, and THORPE), 1840.
$C_{10}H_{17}O$ Geraniol, absorption spectra of (PURVIS), 416.
*l*-Linalool, absorption spectra of (PURVIS), 416.
$C_{10}H_{18}O$ Citronellal, absorption spectra of (PURVIS), 416.
Menthone, absorption spectra of (PURVIS), 413.
α-Terpineol, resolution of, and its esters (FULLER and KENYON), 2304.
$C_{10}H_{18}O_2$ 3-*n*-Butylpropionylacetone, and its copper salt (MORGAN and HOLMES), 763.
$C_{10}H_{18}O_8$ Dimethyl dimethylsaccharate (MACBETH and MACKAY), 1521.
$C_{10}H_{20}O_2$ α-Methylbutaldol (INGOLD), 437.
$C_{10}H_{20}O_5$ Tetramethyl galactose, structure of (HAWORTH, RUELL, and WESTGARTH), 2468.
Tetramethyl γ-mannose (IRVINE and BURT), 1347.
Trimethyl γ-methylmannoside (IRVINE and BURT), 1346.

## 10 III

$C_{10}H_6O_5N_2$ 2:4-Dinitro-α-naphthol, chromammine salts of (KING), 1333.
$C_{10}H_6O_2N_2$ 6-Cyanoindole-2-carboxylic acid (KERMACK), 2289.
$C_{10}H_6O_3S$ 3-Oxy(1)thionaphthen-2-glyoxylic acid, and its salts (HART and SMILES), 878.
$C_{10}H_7O_2N$ β-Nitronaphthalene, reduction of (CUMMING and FERRIER), 1108.
Nitroso-*p*-naphthol, chromammine salt of (KING), 1334.
$C_{10}H_7O_3N$ Nitro-α-naphthols, preparation of (HODGSON and KILNER), 807.
$C_{10}H_7O_4N$ Indole-2:6-dicarboxylic acid (KERMACK), 2288.
$C_{10}H_7O_4N_3$ 2-Nitrophenylglyoxaline-4-carboxylic acids (PYMAN and STANLEY), 2487.
$C_{10}H_7O_6N_3$ 2-*m*-Nitrophenylglyoxaline-4:5-dicarboxylic acid (PYMAN and STANLEY), 2487.
$C_{10}H_7NBr_2$ 6:8-Dibromo-2-methylquinoline (LAWSON, PERKIN, and ROBINSON), 656.
$C_{10}H_8O_3Cl_2$ Methyl 3:5-dichlorocoumarate (DEY and ROW), 562.
$C_{10}H_8O_3Br_2$ Methyl 3:5-dibromocoumarate (DEY and ROW), 562.
$C_{10}H_8O_4N_4$ 4(or 5)-Nitro-5(or -4)-*p*-nitrophenyl-1-methylglyoxalines, and their salts (HAZELDINE, PYMAN, and WINCHESTER), 1439.

$C_{10}H_9ON$ 4-Methoxyquinoline, synthesis of (CLEMO and PERKIN), 1608.
$C_{10}H_9O_2N$ Methoxyindole-3-aldehydes (BLAIKIE and PERKIN), 324.
$C_{10}H_9O_2Br$ 5-Bromo-2-hydroxystyryl methyl ketone (McGOOKIN and HEILBRON), 2104.
$C_{10}H_9O_2N_3$ 4- and 5-Nitrophenyl-1-methylglyoxalines, and their salts (HAZELDINE, PYMAN, and WINCHESTER), 1438.
$C_{10}H_9O_3N$ α-Cyano-β-(3-hydroxyphenyl)-propionic acid (BAKER and LAPWORTH), 2336.
α-Cyano-β-salicylpropionic acid (BAKER and LAPWORTH), 2335.
Methoxyindole-2-carboxylic acids (BLAIKIE and PERKIN), 309.
$C_{10}H_9O_4N$ α-Cyano-β-(2:4-dihydroxyphenyl)-acrylic acid (BAKER and LAPWORTH), 2336.
$C_{10}H_9O_5N$ 2-Nitro-α-methoxycinnamic acid (BLAIKIE and PERKIN), 332.
5-Nitro-4-methylcoumaric acid, and its silver salt (DEY and ROW), 563.
$C_{10}H_9O_6N$ 2-Nitromethoxyphenylpyruvic acids (BLAIKIE and PERKIN), 308.
$C_{10}H_{10}O_3N_2$ Mesoxmono-*p*-tolylamide hydrate (PLOWMAN and WHITELEY), 602.
$C_{10}H_{10}O_5N_2$ Acetoxy-3-nitro-*p*-methoxybenzaldoximes (BRADY and MANJUNATH), 1061.
5-Nitro-*o*-methoxybenz*anti*aldoxime (BRADY and MANJUNATH), 1066.
$C_{10}H_{10}N_3Cl$ Methylpyruvonitrile-*p*-chlorophenylhydrazone (WALKER), 1624.
$C_{10}H_{11}ON$ Methoxyscatoles, and their picrates (BLAIKIE and PERKIN), 329.
$C_{10}H_{11}O_2N$ *o*-Methoxycinnamaldoximes (BRADY and GRAYSON), 1418.
$C_{10}H_{11}O_3N$ 2-Amino-α-methoxycinnamic acid (BLAIKIE and PERKIN), 333.
Benzylcyanoacetic acid (BAKER and LAPWORTH), 2334.
$C_{10}H_{11}O_3N_3$ *iso*Nitrosomalonmono-*p*-tolylamides, isomeric (PLOWMAN and WHITELEY), 598.
$C_{10}H_{11}O_4N$ *p*-Carbethoxyaminobenzoic acid (KING and MURCH), 2602.
4-Methoxy-2-aldehydophenylglycine (BLAIKIE and PERKIN), 326.
$C_{10}H_{11}O_5N$ 6-Nitroacetoveratrone (LAWSON, PERKIN, and ROBINSON), 653.
5-Nitro-3:4-dimethoxyacetophenone (BRADY and MANJUNATH), 1067.
$C_{10}H_{12}O_2N_2$ 1-Carboxy*cyclo*hexane-1-cyanoacetimide (DICKENS, HORTON, and THORPE), 1836.
1-Cyano*cyclo*hexane-1-cyanoacetic acid, salts of (DICKENS, HORTON, and THORPE), 1834.
$C_{10}H_{12}O_4N_2$ 4-Methoxy-2-aldehydophenylglycine oxime (BLAIKIE and PERKIN), 326.
$C_{10}H_{12}O_4N_2$ Mesoxmono-*p*-tolylamide dihydrate (PLOWMAN and WHITELEY), 602.
$C_{10}H_{13}O_2N$ α-Cyano*cyclo*heptylideneacetic acid (DICKENS, HORTON, and THORPE), 1839.
$C_{10}H_{13}O_3N$ 6-Aminoacetoveratrone (LAWSON, PERKIN, and ROBINSON), 653.
$C_{10}H_{13}O_3N_3$ 4-Methoxy-2-aldehydophenylglycineamide oxime (BLAIKIE and PERKIN), 325.
$C_{10}H_{14}ON_4$ Acetone-δ-anilinosemicarbazone (SUTHERLAND and WILSON), 2147.
$C_{10}H_{14}OBr$ αβ-Dibromocamphor, action of sodium methoxide and ethoxide on (BURGESS), 2376.
$C_{10}H_{14}O_3N_2$ α-Carbamyl-1-carboxy*cyclo*hexane-1-acetimide (DICKENS, HORTON, and THORPE), 1837.
1-Carbamyl*cyclo*hexane-1-cyanoacetic acid, and its sodium salt (DICKENS, HORTON, and THORPE), 1835.
$C_{10}H_{15}OCl$ Chlorocamphor, action of hydroxylamine on (BURGESS), 2375.
$C_{10}H_{15}OBr$ Bromocamphor, action of hydroxylamine on (BURGESS), 2375.
$C_{10}H_{15}O_2N$ *d*-Camphorimide, rotatory dispersion of (SINGH and BISWAS), 1895.
1-Carboxy*cyclo*heptane-1-acetimide (DICKENS, HORTON, and THORPE), 1840.

$C_{10}H_{15}O_5N$ α-Carbamyl-1-carboxy*cyclo*hexane-1-acetic acid (DICKENS, HORTON, and THORPE), 1836.

$C_{10}H_{16}O_2Te$ Tellurium 3-*n*-butylpropionylacetone (MORGAN and HOLMES), 764.

Tellurium *n*-heptoylacetone (MORGAN, DREW, and PORTER), 739.

$C_{10}H_{16}O_4S$ Camphorsulphonic acid, salicylatodiethylenediamminocobaltic salts (MORGAN and SMITH), 2002.

$C_{10}H_{17}O_2Cl$ β-Pinene monochlorohydrin (HENDERSON and KERR), 105.

$C_{10}H_{17}O_6Br$ Bromohydroxytricarballylic acid, lactone ester (INGOLD, OLIVER, and THORPE), 2133.

$C_{10}H_{18}O_2Cl_2$ β-Pinene dichlorohydrins (HENDERSON and KERR), 104.

$C_{10}H_{19}O_2N_3$ Methyl *n*-hexyl ketone semioxamazone (WILSON and PICKERING), 1153.

$C_{10}H_{19}O_6N$ Substance, from tetramethylgluconamide and sodium hypochlorite (IRVINE and PRYDE), 1048.

$C_{10}H_{21}O_6N$ Tetramethylgluconamide (IRVINE and PRYDE), 1047.

## 10 IV

$C_{10}H_5O_2N_2Cl_2$ Chloromalein-*p*-chloroanil (CHATTAWAY and PARKES), 467.

$C_{10}H_5O_8N_2S$ 2:4-Dinitro-α-naphthol-7-sulphonic acid, chromammine and cobaltammine salts of (KING), 1333.

$C_{10}H_6O_2NCl$ Chloromaleinanil (CHATTAWAY and PARKES), 466.

$C_{10}H_7O_2N_3Cl_2$ 1-2:4-Dichlorophenyl-3-methyl-4-oximino-5-pyrazolone (CHATTAWAY and STROUTS), 2427.

1-Dichlorophenyl-5-methyl-1:2:3-triazole-4-carboxylic acids (CHATTAWAY, GARTON, and PARKES), 1989.

$C_{10}H_7O_2N_3Br_2$ 1-(2:4-Dibromophenyl)-5-methyl-1:2:3-triazole-4-carboxylic acid (CHATTAWAY, GARTON, and PARKES), 1990.

$C_{10}H_8ONCl$ 3-Chloromethoxyquinolines (BLAIKIE and PERKIN), 325.

$C_{10}H_8ON_2Cl_2$ 1-2:4-Dichlorophenyl-3-methyl-5-pyrazolone, and its hydrochloride (CHATTAWAY and STROUTS), 2427.

$C_{10}H_8O_2N_2Cl$ 1-Chlorophenyl-4-oximino-3-methyl-5-pyrazolones (CHATTAWAY and STROUTS), 2424.

$C_{10}H_8O_5NBr$ Methyl 3-bromo-5-nitrocoumarate (DEY and ROW), 563.

$C_{10}H_9ON_2Cl$ 1-Chlorophenyl-3-methyl-5-pyrazolones, and their hydrochlorides (CHATTAWAY and STROUTS), 2424.

$C_{10}H_9O_2F_2B$ Boron benzoylacetone difluoride (MORGAN and TUNSTALL), 1965.

$C_{10}H_9O_6NHg$ Propionoxymercuri-4-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1056.

$C_{10}H_{10}O_3NBr$ Acetyl derivative of 3-bromo-*p*-methoxybenz*anti*aldoxime (BRADY and MANJUNATH), 1064.

$C_{10}H_{10}O_5NBr$ Ethyl 3-bromo-5-nitrocoumarate (DEY and ROW), 563.

$C_{10}H_{10}NCl_4I$ 8-Methylquinolinium tetrachloroiodide (CHATTAWAY and GARTON), 186.

Quinaldinium tetrachloroiodide (CHATTAWAY and GARTON), 186.

$C_{10}H_{11}ONCl_2$ Dichloroacetoethylanilide, crystallography of (KNAGGS), 1444.

$C_{10}H_{14}O_4Cl_2Ge$ Germanium bisacetylacetone dichloride (MORGAN and DREW), 1264.

$C_{10}H_{14}O_4Br_2Ge$ Germanium bisacetylacetone dibromide (MORGAN and DREW), 1265.

$C_{10}H_{16}ONBr$ α- and α′-Bromocampholenamides (BURGESS), 2379.

$C_{10}H_{16}O_2Cl_2Te$ Tellurium 3-*n*-butylpropionylacetone dichloride (MORGAN and HOLMES), 764.

$C_{10}H_{16}O_2Cl_2Te$ Tellurium *n*-heptoylacetone dichloride (MORGAN, DREW, and PORTER), 739.

$C_{10}H_{17}O_2Cl_2Te$ Tellurium *O*-ethyl*iso*valerylacetone trichloride (MORGAN and DREW), 744.

Tellurium *n*-heptoylacetone trichloride (MORGAN, DREW, and PORTER), 738.

$C_{10}H_{22}O_8Br_6Sn_2$ Tetra-aquostannic bisacetylacetone stannibromide (MORGAN and DREW), 378.

10 V

$C_{10}H_5O_2N_2ClBr$ Chloromalein-*p*-bromoanil (CHATTAWAY and PARKES), 467.

$C_{10}H_{11}ONClI$ Chloroiodoacetoethylanilide (MCKIE), 1076.

$C_{10}H_{11}ONCl_2S$ *n*-Propyl 2:4-dichlorophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1554.

$C_{10}H_{11}ONBr_2S$ *n*-Propyl 2:4-dibromophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{10}H_{12}O_3Cl_2BrS$ *d*-α-Chloro-α′-bromocamphor-π-sulphonyl chloride (MANN and POPE), 916.

10 VI

$C_{10}H_{14}O_3NCl_2BrS$ α-Bromocamphor-π-sulphondichloroamide (MANN and POPE), 913.

$C_{10}H_{15}O_3NClBrS$ *d*-Chlorobromocamphor-π-sulphonamides (MANN and POPE), 915.

## $C_{11}$ Group.

$C_{11}H_8O_7$ Methylcarboxyphthalonic acid (PERKIN and TAPLEY), 2437.

$C_{11}H_8N_2$ 3-Carboline, and its salts (LAWSON, PERKIN, and ROBINSON), 633.

5-Carboline, and its salts (ROBINSON and THORNLEY), 2169.

$C_{11}H_8N_4$ 1-α-Pyridylbenzotriazole (LAWSON, PERKIN, and ROBINSON), 632.

1-γ-Pyridylbenzotriazole, and its hydrochloride (ROBINSON and THORNLEY), 2171.

$C_{11}H_{10}O_2$ 2:6-Dimethylchromone (HALL), 2265.

$C_{11}H_{10}O_3$ 1-Ketohydrindene-3-acetic acid (SPEIGHT, STEVENSON, and THORPE), 2188.

$C_{11}H_{10}O_4$ 7-Hydroxy-3-methoxy-2-methylchromone (ALLAN and ROBINSON), 2193.

$C_{11}H_{10}O_5$ 4:6-Dimethylphthalonic acid, and its hydrate ($+H_2O$) (PERKIN and TAPLEY), 2435.

Dimethylterephthalonic acid (PERKIN and TAPLEY), 2432.

$C_{11}H_{10}O_7$ Methyldicarboxymandelic acid (PERKIN and TAPLEY), 2437.

$C_{11}H_{11}N_3$ *N*-γ-Pyridyl-*o*-phenylenediamine, and its hydrochloride (ROBINSON and THORNLEY), 2170.

$C_{11}H_{12}O$ 1-Keto-2-ethylhydrindene (SPEIGHT, STEVENSON, and THORPE), 2191.

$C_{11}H_{12}O_3$ β-Benzoylbutyric acid (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.

$C_{11}H_{12}O_4$ α-Acetyldihydrocumaric acid, sodium β-sulphonate of (DEY and ROW), 558.

4-Carboxy-2:6-dimethylphenylacetic acid (PERKIN and TAPLEY), 2434.

$C_{11}H_{12}O_5$ Carboxydimethylmandelic acid (PERKIN and TAPLEY), 2433.

$C_{11}H_{13}N_3$ 3:4:5:6-Tetrahydro-5-carboline (ROBINSON and THORNLEY), 2174.

$C_{11}H_{14}O$ Acetomesitylene, oxidation of, with permanganate (PERKIN and TAPLEY), 2428.

$C_{11}H_{14}O_3$ Mesitylglyoxylic acid (PERKIN and TAPLEY), 2432.

$C_{11}H_{14}O_8$ Dimethyl *cyclo*pentanetetracarboxylate ($+H_2O$) (BERNTON, ING, and PERKIN), 1500.

$C_{11}H_{14}S_3$ Benzylidene diethylene trisulphide (RÂY), 1142.

$C_{11}H_{14}S_4$ Benzylidene diethylene tetrasulphide (RÂY), 1142.

$C_{10}H_{15}O_5N$ α-Carbamyl-1-carboxy*cyclo*hexane-1-acetic acid (DICKENS, HORTON, and THORPE), 1836.

$C_{10}H_{16}O_2Te$ Tellurium 3-*n*-butylpropionylacetone (MORGAN and HOLMES), 764.
Tellurium *n*-heptoylacetone (MORGAN, DREW, and PORTER), 739.

$C_{10}H_{16}O_4S$ Camphorsulphonic acid, salicylatodiethylenediamminocobaltic salts (MORGAN and SMITH), 2002.

$C_{10}H_{17}O_2Cl$ β-Pinene monochlorohydrin (HENDERSON and KERR), 105.

$C_{10}H_{17}O_6Br$ Bromohydroxytricarballylic acid, lactone ester (INGOLD, OLIVER, and THORPE), 2133.

$C_{10}H_{18}O_2Cl_2$ β-Pinene dichlorohydrins (HENDERSON and KERR), 104.

$C_{10}H_{19}O_2N_3$ Methyl *n*-hexyl ketone semioxamazone (WILSON and PICKERING), 1153.

$C_{10}H_{19}O_6N$ Substance, from tetramethylgluconamide and sodium hypochlorite (IRVINE and PRYDE), 1048.

$C_{10}H_{21}O_6N$ Tetramethylgluconamide (IRVINE and PRYDE), 1047.

## 10 IV

$C_{10}H_5O_2N_2Cl_2$ Chloromalein-*p*-chloroanil (CHATTAWAY and PARKES), 467.

$C_{10}H_5O_8N_2S$ 2:4-Dinitro-α-naphthol-7-sulphonic acid, chromammine and cobaltammine salts of (KING), 1333.

$C_{10}H_6O_2NCl$ Chloromaleinanil (CHATTAWAY and PARKES), 466.

$C_{10}H_7O_2N_3Cl_2$ 1-2:4-Dichlorophenyl-3-methyl-4-oximino-5-pyrazolone (CHATTAWAY and STROUTS), 2427.
1-Dichlorophenyl-5-methyl-1:2:3-triazole-4-carboxylic acids (CHATTAWAY, GARTON, and PARKES), 1989.

$C_{10}H_7O_2N_3Br_2$ 1-(2:4-Dibromophenyl)-5-methyl-1:2:3-triazole-4-carboxylic acid (CHATTAWAY, GARTON, and PARKES), 1990.

$C_{10}H_8ONCl$ 3-Chloromethoxyquinolines (BLAIKIE and PERKIN), 325.

$C_{10}H_8ON_2Cl_2$ 1-2:4-Dichlorophenyl-3-methyl-5-pyrazolone, and its hydrochloride (CHATTAWAY and STROUTS), 2427.

$C_{10}H_8O_3N_2Cl$ 1-Chlorophenyl-4-oximino-3-methyl-5-pyrazolones (CHATTAWAY and STROUTS), 2424.

$C_{10}H_8O_5NBr$ Methyl 3-bromo-5-nitrocoumarate (DEY and ROW), 563.

$C_{10}H_9ON_2Cl$ 1-Chlorophenyl-3-methyl-5-pyrazolones, and their hydrochlorides (CHATTAWAY and STROUTS), 2424.

$C_{10}H_9O_2F_2B$ Boron benzoylacetone difluoride (MORGAN and TUNSTALL), 1965.

$C_{10}H_9O_6NHg$ Propionoxymercuri-4-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1056.

$C_{10}H_{10}O_3NBr$ Acetyl derivative of 3-bromo-*p*-methoxybenz*anti*aldoxime (BRADY and MANJUNATH), 1064.

$C_{10}H_{10}O_5NBr$ Ethyl 3-bromo-5-nitrocoumarate (DEY and ROW), 563.

$C_{10}H_{10}NCl_4I$ 8-Methylquinolinium tetrachloroiodide (CHATTAWAY and GARTON), 186.
Quinaldinium tetrachloroiodide (CHATTAWAY and GARTON), 186.

$C_{10}H_{11}ONCl_2$ Dichloroacetoethylanilide, crystallography of (KNAGGS), 1444.

$C_{10}H_{14}O_4Cl_2Ge$ Germanium bisacetylacetone dichloride (MORGAN and DREW), 1264.

$C_{10}H_{14}O_4Br_2Ge$ Germanium bisacetylacetone dibromide (MORGAN and DREW), 1265.

$C_{10}H_{16}ONBr$ α- and α′-Bromocampholenamides (BURGESS), 2379.

$C_{10}H_{16}O_2Cl_2Te$ Tellurium 3-*n*-butylpropionylacetone dichloride (MORGAN and HOLMES), 764.

$C_{10}H_{16}O_2Cl_2Te$ Tellurium *n*-heptoylacetone dichloride (MORGAN, DREW, and PORTER), 739.

$C_{10}H_{17}O_2Cl_2Te$ Tellurium *O*-ethyl*iso*valerylacetone trichloride (MORGAN and DREW), 744.

Tellurium *n*-heptoylacetone trichloride (MORGAN, DREW, and PORTER), 738.

$C_{10}H_{22}O_8Br_6Sn_2$ Tetra-aquostannic bisacetylacetone stannibromide (MORGAN and DREW), 378.

10 V

$C_{10}H_5O_2N_2ClBr$ Chloromalein-*p*-bromoanil (CHATTAWAY and PARKES), 467.

$C_{10}H_{11}ONClI$ Chloroiodoacetoethylanilide (McKIE), 1076.

$C_{10}H_{11}ONCl_2S$ *n*-Propyl 2:4-dichlorophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1554.

$C_{10}H_{11}ONBr_2S$ *n*-Propyl 2:4-dibromophenylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{10}H_{12}O_3Cl_2BrS$ *d*-α-Chloro-α′-bromocamphor-π-sulphonyl chloride (MANN and POPE), 916.

10 VI

$C_{10}H_{14}O_3NCl_2BrS$ α-Bromocamphor-π-sulphondichloroamide (MANN and POPE), 913.

$C_{10}H_{15}O_3NClBrS$ *d*-Chlorobromocamphor-π-sulphonamides (MANN and POPE), 915.

## $C_{11}$ Group.

$C_{11}H_8O_7$ Methylcarboxyphthalonic acid (PERKIN and TAPLEY), 2437.

$C_{11}H_9N_2$ 3-Carboline, and its salts (LAWSON, PERKIN, and ROBINSON), 633.

5-Carboline, and its salts (ROBINSON and THORNLEY), 2169.

$C_{11}H_9N_4$ 1-α-Pyridylbenzotriazole (LAWSON, PERKIN, and ROBINSON), 632.

1-γ-Pyridylbenzotriazole, and its hydrochloride (ROBINSON and THORNLEY), 2171.

$C_{11}H_{10}O_2$ 2:6-Dimethylchromone (HALL), 2265.

$C_{11}H_{10}O_3$ 1-Ketohydrindene-3-acetic acid (SPEIGHT, STEVENSON, and THORPE), 2188.

$C_{11}H_{10}O_4$ 7-Hydroxy-3-methoxy-2-methylchromone (ALLAN and ROBINSON), 2193.

$C_{11}H_{10}O_5$ 4:6-Dimethylphthalonic acid, and its hydrate ($+H_2O$) (PERKIN and TAPLEY), 2435.

Dimethylterephthalonic acid (PERKIN and TAPLEY), 2432.

$C_{11}H_{10}O_7$ Methyldicarboxymandelic acid (PERKIN and TAPLEY), 2437.

$C_{11}H_{11}N_3$ *N*-γ-Pyridyl-*o*-phenylenediamine, and its hydrochloride (ROBINSON and THORNLEY), 2170.

$C_{11}H_{12}O$ 1-Keto-2-ethylhydrindene (SPEIGHT, STEVENSON, and THORPE), 2191.

$C_{11}H_{12}O_3$ β-Benzoylbutyric acid (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.

$C_{11}H_{12}O_4$ α-Acetyldihydrocoumaric acid, sodium β-sulphonate of (DEY and ROW), 558.

4-Carboxy-2:6-dimethylphenylacetic acid (PERKIN and TAPLEY), 2434.

$C_{11}H_{12}O_5$ Carboxydimethylmandelic acid (PERKIN and TAPLEY), 2433.

$C_{11}H_{12}N_2$ 3:4:5:6-Tetrahydro-5-carboline (ROBINSON and THORNLEY), 2174.

$C_{11}H_{14}O$ Acetomesitylene, oxidation of, with permanganate (PERKIN and TAPLEY), 2428.

$C_{11}H_{14}O_3$ Mesitylglyoxylic acid (PERKIN and TAPLEY), 2432.

$C_{11}H_{14}O_8$ Dimethyl *cyclo*pentanetetracarboxylate ($+H_2O$) (BERNTON, ING, and PERKIN), 1500.

$C_{11}H_{14}S_3$ Benzylidene diethylene trisulphide (RÂY), 1142.

$C_{11}H_{14}S_4$ Benzylidene diethylene tetrasulphide (RÂY), 1142.

$C_{11}H_{20}O_4$ *n*-Octylmalonic acid (ROBINSON), 228.
$C_{11}H_{22}O_2$ Undecoic acid, rhythmic crystallisation of (GARNER and RANDALL), 369.
$C_{11}H_{22}O_3$ Ethyl *d*-β-octyl carbonate, rotatory power of (HUNTER), 1394.
$C_{11}H_{22}O_6$ Tetramethyl methylgalactoside (HAWORTH, RUELL, and WESTGARTH), 2472.
Tetramethyl γ-methylmannoside (IRVINE and BURT), 1346.
$C_{11}H_{22}O_7$ Methyl tetramethyl gluconate (PRYDE), 520.

## 11 III

$C_{11}H_{10}O_2N_2$ 3-Amino-2-methylquinoline-4-carboxylic acid (LAWSON, PERKIN, and ROBINSON), 635.
$C_{11}H_{10}O_3Br_2$ Ethyl 3:5-dibromocoumarate (DEY and ROW), 562.
$C_{11}H_{10}O_4N_2$ Nitro-1-acetyl-5-methoxyindoles (BLAIKIE and PERKIN), 323.
$C_{11}H_{11}O_2N$ 1-Acetyl-5-methoxyindole (BLAIKIE and PERKIN), 323.
$C_{11}H_{11}O_2N_3$ 1-*o*-Tolyl-5-methyl-1:2:3-triazole-4-carboxylic acid (CHATTAWAY, GARTON, and PARKES), 1989.
$C_{11}H_{11}O_3N$ α-Cyano-β-anisylpropionic acid (BAKER and LAPWORTH), 2335.
4-Hydroxy-6:7-dimethoxyquinoline (LAWSON, PERKIN, and ROBINSON), 655.
Methyl methoxyindole-2-carboxylates (BLAIKIE and PERKIN), 309.
$C_{11}H_{11}O_3N_3$ 1-Ketohydrindene-3-carboxylic acid semicarbazone (SPEIGHT, STEVENSON, and THORPE), 2190.
$C_{11}H_{11}O_5N$ Methyl 2-nitro-α-methoxycinnamate (BLAIKIE and PERKIN), 333.
$C_{11}H_{11}O_6N$ 2-Nitrodimethoxycinnamic acids (BLAIKIE and PERKIN), 330.
$C_{11}H_{12}O_4N_2$ Acetylnitro-3:4-dimethoxybenzaldoximes (BRADY and MANJUNATH), 1066.
$C_{11}H_{13}O_3N$ Methyl 2-amino-α-methoxycinnamate (BLAIKIE and PERKIN), 333.
$C_{11}H_{13}O_3N_3$ *iso*Nitrosomalonmono-*p*-tolylamide methyl ethers (PLOWMAN and WHITELEY), 600.
$C_{11}H_{13}O_4N$ 2-Aminodimethoxycinnamic acids (BLAIKIE and PERKIN), 331.
Methyl *p*-carbethoxyaminobenzoate (KING and MURCH), 2603.
$C_{11}H_{13}N_2I$ 4(or 5)-Phenyl-1:3-dimethylglyoxalinium iodide (HAZELDINE, PYMAN, and WINCHESTER), 1437.
$C_{11}H_{14}O_2N_2$ 1-Carboxy*cyclo*heptane-1-cyanoacetimide (DICKENS, HORTON, and THORPE), 1840.
$C_{11}H_{14}O_3N_2$ α-Ketobutyric acid methoxyphenylhydrazones (BLAIKIE and PERKIN), 314.
$C_{11}H_{15}O_6N$ Nitro-2:3-dimethoxybenzaldehyde dimethyl acetals (PERKIN, ROBINSON, and STOYLE), 2358.
$C_{11}H_{15}NBr_2$ 1-Bromo*cyclo*hexane-2-pyridinium bromide (BARNETT, COOK, and PECK), 1038.
$C_{11}H_{17}O_2Br$ Methyl α-bromocampholenate (BURGESS), 2378.

## 11 IV

$C_{11}H_7O_3NBr_2$ 6:8-Dibromo-2-methylquinoline-4-carboxylic acid (LAWSON, PERKIN, and ROBINSON), 656.
$C_{11}H_8O_3NBr$ 8-Bromo-6-acetylaminocoumarin (DEY and ROW), 561.
$C_{11}H_8O_3NI$ 8-Iodo-6-acetylaminocoumarin (DEY and ROW), 561.
$C_{11}H_9O_8NHg_2$ Diacetoxydimercuri-2-nitro-3-hydroxybenzaldehyde (HENRY and SHARP), 1058.
$C_{11}H_{10}ON_2Cl_2$ 1-2:4-Dichlorophenyl-2:3-dimethyl-5-pyrazolone (CHATTAWAY and STROUTS), 2427.
$C_{11}H_{11}ON_2Cl$ 1-Chlorophenyl-2:3-dimethyl-5-pyrazolones (CHATTAWAY and STROUTS), 2424.
$C_{11}H_{12}ONI$ 4-Methoxyquinoline methiodide (CLEMO and PERKIN), 1618.

$C_{11}H_{12}O_4NBr$ Acetyl-6-bromo-3:4-dimethoxybenz*anti*aldoxime (Brady and Manjunath), 1067.

$C_{11}H_{13}ONS$ *n*-Butyl phenylthiocarbamate (Chattaway, Hardy, and Watts), 1556.

$C_{11}H_{21}O_3N_4Co$ Salicylatodiethylenediamminecobaltic hydroxide, salts of (Morgan and Smith), 2000.

## $C_{12}$ Group.

$C_{12}H_8O_7$ Diacetyltartaric anhydride, action of, on aromatic amines and hydrazines (Chattaway and Parkes), 466.

$C_{12}H_9N$ Pyridofluorene (Mills, Palmer, and Tomkinson), 2369.

$C_{12}H_{10}O_4$ Cinnamylidenemalonic acid, photochemical transformation of (Bowen, Hartley, Scott, and Watts), 1220.

Piperic acid, absorption spectra of (Purvis), 410.

$C_{12}H_{10}O_5$ 5-Phenyl-2:3-dihydrofuran-2:3-dicarboxylic acid (Ing and Perkin), 1827.

$C_{12}H_{10}N_2$ Harmine (Lawson, Perkin, and Robinson), 626; (Nishikawa, Perkin, and Robinson), 657.

5-Methyl-5-*iso*carboline (Robinson and Thornley), 2173.

$C_{12}H_{12}O_2$ α-Phenyl-γ-methyl-Δ$^{\alpha}$-pentinen-γ-ol-δ-one (Wilson and Hyslop), 1557.

$C_{12}H_{12}O_4$ 3:7-Dimethoxy-2-methylchromone (Allan and Robinson), 2194.

$C_{12}H_{12}O_5$ α-Benzoylethylmalonic acid (Higginbotham, Lapworth, and Simpson), 2342.

$C_{12}H_{12}N_2$ Hydrazobenzene, hydroferricyanide of (Cumming), 2542.

$C_{12}H_{14}O_{12}$ Dicarbomethoxy mannitol dicarbonate (Allpress and Haworth), 1231.

$C_{12}H_{15}N$ Hexahydrocarbazole (Perkin and Plant), 1512.

$C_{12}H_{17}N$ Octahydrocarbazole, and its picrate (Perkin and Plant), 1503.

$C_{12}H_{19}N$ Decahydrocarbazole, and its picrate (Perkin and Plant), 1509.

$C_{12}H_{20}O_9$ Tricarbethoxyglycerol (Allpress and Maw), 2263.

$C_{12}H_{20}N_2$ β-Diethylaminoethylaniline (Clemo and Perkin), 1809.

$C_{12}H_{21}N$ Dodecahydrocarbazole, and its picrate (Perkin and Plant), 1509.

$C_{12}H_{22}O_6$ *d-sec.*-Octyl tartrate, preparation and rotation of (Patterson and Buchanan), 1475.

$C_{12}H_{22}O_{11}$ Lactose, estimation of (Knecht and Hibbert), 2011.

Maltose, estimation of (Knecht and Hibbert), 2011.

Sucrose, rotatory dispersion of (Lowry and Richards), 2511; mutarotation lag in the inversion of (Pennycuick), 2049; hydrogen-ion concentration in solutions of (Taylor and Bomford), 2016; effect of catalysts on carbonisation of (Lessing and Banks), 2347; estimation of (Knecht and Hibbert), 2011.

$C_{12}H_{24}O_7$ Methyl pentamethyl gluconate (Pryde), 520.

### 12 III

$C_{12}H_5O_{12}N_7$ Dipicrylamide, chromammine salts of (King), 1333.

$C_{12}H_6O_2Cl_2$ 1:8-Naphthalyl chloride, preparation and properties of (Mason), 2116.

$C_{12}H_7O_3N$ 2-Methylquinoline-3:4-dicarboxylic anhydride (Lawson, Perkin, and Robinson), 634.

$C_{12}H_8O_2N_2$ 2-Methylquinoline-3:4-dicarboxylimide (Lawson, Perkin, and Robinson), 634.

$C_{12}H_8NI$ 3-Iodocarbazole (Tucker), 1148.

$C_{12}H_8N_2Cl$ Carbazole-3-diazonium chloride (+ $3H_2O$) (Tucker), 1145.

$C_{12}H_8N_2Br$ Carbazole-3-diazonium bromide (+ $2H_2O$) (Tucker), 1146.

$C_{12}H_8N_2I$ Carbazole-3-diazonium iodide (+ $H_2O$) (Tucker), 1147.

$C_{12}H_9O_3N$ 6-Hydroxyquinoline-5-β-acrylic acid, and its silver salt (Dey and Row), 564.

$C_{12}H_{10}O_2N_2$ Ethyl 6-cyanoindole-2-carboxylate (KERMACK), 2289.
10-Methoxy-5-keto-4:5-dihydroindolediazine (1:4) (BLAIKIE and PERKIN), 318.
$C_{12}H_{10}O_3N_2$ Benzeneazo*allo*maltol (YABUTA), 579.
$C_{12}H_{10}O_5N_2$ Ethyl 2-nitro-4-cyanophenylpyruvate (KERMACK), 2288.
$C_{12}H_{10}ClAs$ Diphenylarsenious chloride, dimorphism of (GIBSON and VINING), 910.
$C_{12}H_{11}O_5N$ 4-Hydroxy-6:7-dimethoxyquinoline-2-carboxylic acid (LAWSON, PERKIN, and ROBINSON), 654.
$C_{12}H_{11}O_6N$ 6-Nitroveratroylpyruvic acid (LAWSON, PERKIN, and ROBINSON), 654.
$C_{12}H_{12}O_2N_2$ Ketotetrahydronorharmine (NISHIKAWA, PERKIN, and ROBINSON), 661.
$C_{12}H_{13}O_3N$ Acetyl-*o*-methoxycinnamaldoximes (BRADY and GRAYSON), 1418.
Ethyl methoxyindole-2-carboxylates (BLAIKIE and PERKIN), 309.
Methyl methoxyscatole-2-carboxylates (BLAIKIE and PERKIN), 315.
$C_{12}H_{13}O_3N_3$ 1-Ketohydrindene-3-acetic acid semicarbazone (SPEIGHT, STEVENSON, and THORPE), 2188.
$C_{12}H_{13}O_4N_3$ Acetyl derivative of *iso*nitrosomalonmono-*p*-tolylamide (PLOWMAN and WHITELEY), 603.
$C_{12}H_{13}O_5N$ Phenacylsuccinic acid oxime (ING and PERKIN), 1828.
$C_{12}H_{13}O_6N$ Methyl 2-nitro-α:5-dimethoxycinnamate (BLAIKIE and PERKIN), 331.
$C_{12}H_{14}O_3N_2$ 6-Methoxy-3-β-aminoethylindole-2-carboxylic acid (NISHIKAWA, PERKIN, and ROBINSON), 662.
$C_{12}H_{15}ON$ Physostigmol ethyl ether, and its picrate (STEDMAN), 1375.
$C_{12}H_{15}ON_3$ 1-Keto-2-ethylhydrindene semicarbazone (SPEIGHT, STEVENSON, and THORPE). 2191.
$C_{12}H_{15}O_3N_3$ β-Benzoylbutyric acid semicarbazone (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2343.
$C_{12}H_{15}O_4N$ Carbethoxyamino-*p*-methoxyacetophenone (RIDGWAY and ROBINSON), 2241.
Methyl 2-amino-α:5-dimethoxycinnamate (BLAIKIE and PERKIN), 331.
$C_{12}H_{15}O_6N$ Methyl 2-cyano*cyclo*pentane-1:2:3-tricarboxylate (BERNTON, ING, and PERKIN), 1499.
$C_{12}H_{16}O_2N_2$ Ethyl 1-cyano*cyclo*hexane-1-cyanoacetate (DICKENS, HORTON, and THORPE), 1834.
$C_{12}H_{17}O_6Br$ Ethyl α-bromoaconitate (INGOLD, OLIVER, and THORPE), 2134.
$C_{12}H_{19}O_2Br$ Ethyl α-bromocampholenate (BURGESS), 2378.

## 12 IV

$C_{12}H_6O_2Cl_4S_2$ 2:5:2′:5-Tetrachlorodiphenyl disulphoxide (SMILES and GIBSON), 180.
$C_{12}H_6N_4Cl_{10}Pb$ 2:4-Dichlorobenzenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.
$C_{12}H_6O_7N_3Br$ 2-Bromo-4:6-dinitrodiphenylamine (SANÉ and JOSHI), 2483.
$C_{12}H_6N_4Cl_6Pb$ Diphenyl-4:4′-bisdiazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1986.
$C_{12}H_8N_4Cl_8I_2$ Diphenyl-4:4′-bisdiazonium octachlorodi-iodide (CHATTAWAY, GARTON, and PARKES), 1984.
$C_{12}H_{10}O_2NAs$ Phenarsazinic acid, and its salts (BURTON and GIBSON), 2276.
$C_{12}H_{11}O_2NSe$ Cyanoselenium ω-phenylacetylacetone (MORGAN and PORTER), 1273.
$C_{12}H_{11}O_2N_3Cl_2$ Ethyl 1-(2:4-dichlorophenyl)-5-methyl-1:2:3-triazole-4-carboxylate (CHATTAWAY, GARTON, and PARKES), 1989.
$C_{12}H_{11}O_2N_3Br_2$ Ethyl 1-(2:4-dibromophenyl)-5-methyl-1:2:3-triazole-4-carboxylate (CHATTAWAY, GARTON, and PARKES), 1990.
$C_{12}H_{12}O_2N_2S_2$ Aniline *p*-disulphoxide (BERE and SMILES), 2359.

$C_{12}H_{17}ONS$ *n*-Butyl *p*-tolylthiocarbamate (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{12}H_{18}O_4Cl_2Ge$ Germanium bispropionylacetone dichloride (MORGAN and DREW), 1265.

$C_{12}H_4N_4Cl_6Br_6Pb$ 2:4:6-Tribromobenzenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.

$C_{12}H_6N_4Cl_6Br_4Pb$ 2:4-Dibromobenzenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.

$C_{12}H_7O_2NCl_2S_2$ 2:5-Dichloro-3′-nitrodiphenyl disulphide (SMILES and GIBSON), 182.

$C_{12}H_8O_4N_6Cl_6Pb$ *o*-Nitrobenzenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.

$C_{12}H_8N_4Cl_6Br_2Pb$ *p*-Bromobenzenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.

$C_{12}H_{19}O_3NClBrS$ *d*-α-Bromocamphor-π-sulphonethylchloroamide (MANN and POPE), 913.

## $C_{13}$ Group.

$C_{13}H_8O_6$ Benzoylcomenic acid (YABUTA), 581.

$C_{13}H_{10}O_3$ α-Naphthacoumaric acid, and its silver salt (DEY and ROW), 563

$C_{13}H_{10}O_4$ Benzoyl*allo*maltol (YABUTA), 579.

$C_{13}H_{10}O_5$ 2:4:2′:4′-Tetrahydroxybenzophenone, preparation of (SHOESMITH and HALDANE), 113.

$C_{13}H_{10}N_2$ 9-Aminoacridine (CLEMO, PERKIN, and ROBINSON), 1786.

$C_{13}H_{12}O_2$ α-Naphthyl methoxymethyl ketone (RIDGWAY and ROBINSON), 219.

$C_{13}H_{12}O_5$ 7-Acetoxy-3-methoxy-2-methylchromone (ALLAN and ROBINSON), 2193.

Carbethoxy-derivative of 7-hydroxy-4-methylcoumarin (BARGER and EATON), 2410.

$C_{13}H_{12}O_8$ α-Hydroxy-γ-benzoyltricarballylic acid (ING and PERKIN), 1827.

$C_{13}H_{12}N_2$ 9-Amino-5:10-dihydroacridine (CLEMO, PERKIN, and ROBINSON), 1785.

Diphenylformamidine, condensation of, with phenols (SHOESMITH and HALDANE), 2405.

$C_{13}H_{13}N$ Tetrahydroacridine, and its salts (PERKIN and SEDGWICK), 2446.

$C_{13}H_{14}O_2$ 4-Acetonyl-2-methyl-γ-pyran (FORSTER and HEILBRON), 343.

$C_{13}H_{14}O_5$ Dimethyl dimethylphthalonate (PERKIN and TAPLEY), 2436.

Dimethyl dimethylterephthalonate (PERKIN and TAPLEY), 2433.

$C_{13}H_{14}N_2$ Aminotetrahydroacridine, and its salts (PERKIN and SEDGWICK), 2447.

$C_{13}H_{16}O_4$ Dimethyl 4-carboxy-2:6-dimethylphenylacetate (PERKIN and TAPLEY), 2434.

$C_{13}H_{16}O_{13}$ Tricarbomethoxy galactose carbonate (ALLPRESS and HAWORTH), 1230.

$C_{13}H_{17}N$ 9-Methylhexahydrocarbazole (PERKIN and PLANT), 1512.

Octahydroacridine, and its salts (PERKIN and SEDGWICK), 2449.

$C_{13}H_{18}O$ 2-β-Phenylethyltetrahydropyran (SHAW), 1933.

$C_{13}H_{18}O_8$ Methyl *cyclo*pentane-1:2:2:3-tetracarboxylate (BERNTON, ING, and PERKIN), 1497.

$C_{13}H_{19}N$ 9-Methyloctahydrocarbazole, and its picrate (PERKIN and PLANT), 1509.

$C_{13}H_{21}N$ 9-Methyldecahydrocarbazole, and its picrate (PERKIN and PLANT), 1510.

$C_{13}H_{23}N$ 9-Methyldodecahydrocarbazole, and its picrate (PERKIN and PLANT), 1510.

$C_{13}H_{24}O_2$ *n*-Decoylacetone, and its copper salt (MORGAN and HOLMES), 764.

$C_{13}H_{28}O$ *n*-Decyldimethylcarbinol (ROBINSON), 230.

## 13 III


$C_{13}H_8O_2I_4$ Tetraiododihydroxybenzophenone (SPIERS), 458.

$C_{13}H_7ON_3$ Acridonediazole (CLEMO, PERKIN, and ROBINSON), 1771.

$C_{13}H_9O_5N_3$ 3:3-Dinitrobenzophenone, preparation of (BARNETT and MATTHEWS), 767.

$C_{13}H_8O_7N_4$ Nitrobenz*syn*aldoximes 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.

$C_{13}H_8NCl$ 9-Chloroacridine (CLEMO, PERKIN, and ROBINSON), 1775.

$C_{13}H_8N_2Cl_2$ *pp'*-Dichlorodiphenylcarbodi-imide (INGOLD), 100.

$C_{13}H_9O_2N_3$ 1-*o*-Carboxyphenyl-1:2:3-benztriazole (CLEMO, PERKIN, and ROBINSON), 1780.

$C_{13}H_9O_2As$ *o*-Carboxydiphenylarsinous anhydride (AESCHLIMANN and MCCLELAND), 2032.

$C_{13}H_9O_3As$ *o*-Carboxydiphenylarsinic anhydride (AESCHLIMANN and MCCLELAND), 2032.

$C_{13}H_9O_4Cl$ 5-Benzoyloxy-2-chloromethyl-γ-pyrone (YABUTA), 578.

$C_{13}H_9O_5N$ 4-Nitro-α-naphthacoumaric acid, and its silver salt (DEY and ROW), 564.

$C_{13}H_9O_6N_3$ *p*-Hydroxybenz*syn*aldoxime monodinitrophenyl ether (BRADY and TRUSZKOWSKI), 1092.

$C_{13}H_9N_2Cl$ Phenyl-*p*-chlorophenylcarbodi-imide (INGOLD), 97.

$C_{13}H_9N_2Br$ *p*-Bromodiphenylcarbodi-imide (INGOLD), 98.

$C_{13}H_{10}ON_2$ Anhydro-2'-aminodiphenylamine-6-carboxylic acid (CLEMO, PERKIN, and ROBINSON), 1779.

$C_{13}H_{10}O_2N_4$ 7-Nitro-1-phenyl-4-(or 6-)methyl-1:2:3-triazole (BRADY, HEWETSON, and KLEIN), 2404.

$C_{13}H_{10}O_3N_2$ *p*-Nitrobenzophenoneoximes (BRADY and MEHTA), 2300.

$C_{13}H_{10}O_5N_4$ *o*-Aminobenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.

$C_{13}H_{10}NCl$ 9-Chlorodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1775.

$C_{13}H_{10}Cl_2S_2$ 2:5-Dichloro-4'-methyldiphenyl disulphide (SMILES and GIBSON), 182.

$C_{13}H_{11}O_4N$ *allo*Maltol phenylcarbamate (YABUTA), 579.

$C_{13}H_{11}O_4As$ Benzophenone-*o*-arsinic acid (AESCHLIMANN and MCCLELAND), 2031.

$C_{13}H_{12}O_2N_2$ 2'-Aminodiphenylamine-6-carboxylic acid, and its hydrochloride (CLEMO, PERKIN, and ROBINSON), 1779.

Methoxy-5-keto-4-methyl-4:5-dihydroindolediazines(1:4) (BLAIKIE and PERKIN), 317.

Nitrotetrahydroacridine (PERKIN and SEDGWICK), 2446.

$C_{13}H_{12}O_2N_4$ Methoxy-3-keto-4-methyl-3:4-dihydro-4-carbolines (BLAIKIE and PERKIN), 317.

$C_{13}H_{12}O_3N_2$ Nitrotetrahydroacridones (PERKIN and SEDGWICK), 2442.

$C_{13}H_{12}NCl$ 5-Chlorotetrahydroacridine, and its hydrochloride (PERKIN and SEDGWICK), 2446.

$C_{13}H_{13}ON$ Tetrahydroacridone, and its salts (PERKIN and SEDGWICK), 2441.

$C_{13}H_{13}O_2N_3$ 6-Nitro-2-amino-3-(or 5-)methyldiphenylamine (BRADY, HEWETSON, and KLEIN), 2404.

$C_{13}H_{14}ON_2$ 5-Acetyl-3:4:5:6-tetrahydro-5-carboline (ROBINSON and THORNLEY), 2174.

Aminotetrahydroacridones, and their hydrochlorides (PERKIN and SEDGWICK), 2445.

Harmaline (LAWSON, PERKIN, and ROBINSON), 626; (NISHIKAWA, PERKIN, and ROBINSON), 657.

$C_{13}H_{14}O_4N_2$ *cyclo*Hexylidenenitroanthranilic acids (PERKIN and SEDGWICK), 2443.

$C_{13}H_{16}O_2N_2$ α-Phenyl-γ-methyl-$\Delta_\alpha$-pentinen-γ-ol-δ-one semicarbazone (WILSON and HYSLOP), 1557.

$C_{13}H_{15}O_3N$ 4-Acetoxytetrahydroquinoline (CLEMO and PERKIN), 1621.

Methoxyscatole-2-carboxylic acids (BLAIKIE and PERKIN), 314.

$C_{13}H_{15}O_4N$ Ethyl 2-nitro-α:5-dimethoxycinnamate (BLAIKIE and PERKIN), 331.

$C_{13}H_{16}O_2N_2$ Nitro-octahydroacridine, and its hydrochloride (PERKIN and SEDGWICK), 2450.

$C_{13}H_{17}ON_3$ Mesityl oxide δ-phenylsemicarbazones (WILSON and MACAULAY), 842.

$C_{13}H_{17}O_4N$ Ethyl 2-cyano*cyclo*propane-1:2:3-tricarboxylate (ING and PERKIN), 1826.

$C_{13}H_{18}O_2N_2$ Ethyl 1-cyano*cyclo*heptane-1-cyanoacetate (DICKENS, HORTON, and THORPE), 1839.

$C_{13}H_{19}O_3N$ Ethyl α-ketobutyrate *m*-methoxyphenylhydrazone (BLAIKIE and PERKIN), 315.

$C_{13}H_{19}ON$ Decahydroacridone (PERKIN and SEDGWICK), 2445.

$C_{13}H_{22}O_3Te$ Tellurium *n*-decoylacetone (MORGAN and HOLMES), 765.

$C_{13}H_{20}OS$ Ethylthiolmethylenecamphors (MANN and POPE), 917.

## 13 IV

$C_{13}H_8O_2N_2S$ 9-Nitrothioacridone (CLEMO, PERKIN, and ROBINSON), 1784.

$C_{13}H_9OCl_2As$ Benzophenone-*o*-dichloroarsine (AESCHLIMANN and MCCLELAND), 2030.

$C_{13}H_9O_3Br_3S$ 2:4:6-Tribromophenyl *p*-toluenesulphonate (SANÉ and JOSHI), 2482.

$C_{13}H_{10}ONCl$ *N*-*p*-Chlorophenylbenzaldoxime (INGOLD and WEAVER), 1462.

$C_{13}H_{10}ON_2Cl_2$ *pp'*-Dichlorodiphenylcarbamide (INGOLD), 100.

2:4-Di-*p*-chlorophenylmethylene-1:2:4-oxadi-imine (INGOLD), 95.

$C_{13}H_{10}ON_2Br_2$ *pp'*-Dibromodiphenylcarbamide (INGOLD), 101.

2:4-Di-*p*-bromophenylmethylene-1:2:4-oxadi-imine (INGOLD), 95.

$C_{13}H_{10}O_2ClAs$ *o*-Carboxydiphenylchloroarsine (AESCHLIMANN and MCCLELAND), 2032.

$C_{13}H_{10}N_2Cl_2S$ 2:4-Dichlorodiphenylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{13}H_{10}N_2Br_2S$ 2:4-Dibromodiphenylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{13}H_{11}ON_4Cl$ 2-Phenyl-4-*p*-chlorophenylmethylene-1:2:4-oxadi-imine (INGOLD), 94.

$C_{13}H_{11}ON_2Br$ 2-Phenyl-4-*p*-bromophenylmethylene-1:2:4-oxadi-imine (INGOLD), 95.

$C_{13}H_{11}O_2F_2B$ Boron dibenzoylmethane difluoride (MORGAN and TUNSTALL), 1966.

$C_{13}H_{11}O_3NS$ Benzanilide-*p*-sulphinic acid (BERE and SMILES), 2362.

$C_{13}O_{11}O_6N_2As$ Nitrobenzoyl-*p*-aminophenylarsinic acids, and their salts (KING and MURCH), 2602.

$C_{13}H_{12}O_4NAs$ Benzoyl-*p*-aminophenylarsinic acid, and its ammonium salt (KING and MURCH), 2601.

$C_{13}H_{13}ON_2Cl$ 1-*m*-Chlorophenyl-3-methyl-4-*iso*propylidene-5-pyrazolone (CHATTAWAY and STROUTS), 2425.

$C_{13}H_{13}O_2NSe$ Cyanoselenium β-phenylpropionylacetone (MORGAN and PORTER), 1275.

$C_{13}H_{13}O_4NS$ α- and *p*-Naphthalenesulphonylalanines, and their salts (COLLES and GIBSON), 2506.

$C_{13}H_{13}O_4N_2As$ Aminobenzoyl-*p*-aminophenylarsinic acids, and their salts (King and Murch), 2604.

$C_{13}H_{13}O_8NHg_2$ 2:4-Dipropionoxydimercuri-6-nitro-3-hydroxybenzaldehyde (Henry and Sharp), 1054.

$C_{13}H_{14}O_4N_2S$ 5-Carboline methosulphate (Robinson and Thornley), 2173.

$C_{13}H_{14}O_7N_2As$ *s*-Diphenylcarbamide-4:4′-diarsinic acid (King and Murch), 2609.

$C_{13}H_{14}O_{12}Cl_{10}Sn_2$ Pentadichloroacetyl derivative of methylstannonic acid (Lambourne), 2014.

$C_{13}H_{22}O_2Cl_2Te$ Tellurium *n*-decoylacetone dichloride (Morgan and Holmes), 765.

**13 V**

$C_{13}H_9ON_2ClBr$ *N*-Hydroxy-*N*- and -*N*′-*p*-chlorophenyl-*p*-bromophenylformamidines, and their salts (Farrow and Ingold), 2550.

$C_{13}H_9O_5NBr_2S$ Dibromonitrophenyl *p*-toluenesulphonates (Sané and Joshi), 2482.

$C_{13}H_9O_7N_2BrS$ 2-Bromo-4:6-dinitrophenyl *p*-toluenesulphonate (Sané and Joshi), 2482.

$C_{13}H_{10}ON_2ClBr$ 2-*p*-Chlorophenyl-4-*p*-bromophenylmethylene-1:2:4-oxadi-imine (Ingold), 101.

$C_{13}H_{11}O_4N_4ClS$ Substance, and its picrate, from 1-chloro-2:4-dinitrobenzene and phenylthiocarbamide (Taylor and Dixon), 247.

$C_{13}H_{12}O_2N_2ClBr$ *N*-Hydroxy-*N*′-*p*-chlorophenyl-*N*-*p*-bromophenylformamidine hydrate (Farrow and Ingold), 2552.

## $C_{14}$ Group.

$C_{14}H_8O_4$ Alizarin, chromammine salt of (King), 1335.

$C_{14}H_{11}N$ 2-Stilbazole, preparation and reduction of (Shaw), 1932.

9-Vinylcarbazole (Clemo and Perkin), 1811.

$C_{14}H_{12}N_2$ Anilinophenylacetonitrile, action of ethyl ethylidenemalonate with (Higginbotham, Lapworth, and Simpson), 2339.

Phenyl-*p*-tolylcarbodi-imide (Ingold), 96.

$C_{14}H_{13}N$ 1:3-Dimethylpyridofluorene (Mills, Palmer, and Tomkinson), 2369.

$C_{14}H_{14}N_2$ 6-Amino-9-methyl-5:10-dihydroacridine (Clemo, Perkin, and Robinson), 1774.

$C_{14}H_{14}S_5$ Dibenzyl pentasulphide, and its additive compound with piperidine (Thomas and Riding), 2217.

$C_{14}H_{15}N$ 9-Vinyltetrahydrocarbazole (Clemo and Perkin), 1813.

$C_{14}H_{15}N_3$ Dimethylaminoazobenzene, hydroferricyanide of (Cumming), 2542.

$C_{14}H_{16}O_2$ Methoxy-4-acetonyl-2-methyl-γ-pyrans (Forster and Heilbron), 346.

$C_{14}H_{16}N_2$ *o*-Hydrazotoluene hydroferricyanide (Cumming), 2542.

$C_{14}H_{19}N$ 10-Methyloctahydroacridine, and its picrate (Perkin and Sedgwick), 2449.

$C_{14}H_{20}O_7$ Ethyl 5-methyl-2:3-dihydrofuran-2:3:4-tricarboxylate (Ing and Perkin), 1829.

$C_{14}H_{20}O_{10}$ Tetra-acetyl *d*-glucose, mutarotation of (Baker, Ingold, and Thorpe), 286.

$C_{14}H_{28}O_{14}$ Tetracarbomethoxy fructose (Allpress and Haworth), 1228.

Tetracarbomethoxy galactose (Allpress and Haworth), 1230.

Tetracarbomethoxy glucose (Allpress and Haworth), 1230.

$C_{14}H_{21}N$ 9-Ethyloctahydrocarbazole, and its picrate (Perkin and Plant), 1511.

$C_{14}H_{22}O_{10}$ Dicarbethoxydiethyl tartrate (Allpress and Maw), 2263.

$C_{14}H_{23}N$ 9-Ethyldecahydrocarbazole, and its picrate (Perkin and Plant), 1511.

$C_{14}H_{24}O_4$ 2-Acetyl-3-*o*-methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one (HEILBRON and FORSTER), 2068.

$C_{14}H_{25}N$ 9-Ethyldodecahydrocarbazole, and its picrate (PERKIN and PLANT), 1512.

## 14 III

$C_{14}H_8O_5S$ Thionylalizarin (GREEN), 1450.

$C_{14}H_7O_2Br_3$ 9:10-Dibromophenanthrene-2-sulphonyl bromide (HENSTOCK), 1299.

$C_{14}H_8O_3Cl_2$ *p*-Chlorobenzoic anhydride (RULE and PATERSON), 2161.

$C_{14}H_8ClBr$ 9-Chloro-10-bromoanthracene (BARNETT and COOK), 1086.

$C_{14}H_9O_4As$ *oo'*-Dicarboxydiphenylarsinous anhydride (AESCHLIMANN and MCCLELAND), 2034.

$C_{14}H_9O_5As$ *oo'*-Dicarboxydiphenylarsinic anhydride (AESCHLIMANN and MCCLELAND), 2034.

$C_{14}H_9O_7N_3$ 3:4-Methylenedioxybenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.

$C_{14}H_9O_{12}N_7$ 2:4:6:2':4':6'-Hexanitro-3:3'-dimethyldiphenylamine (BRADY, HEWETSON, and KLEIN), 2404.

$C_{14}H_{10}O_2N_2$ 2-Methylpyridine-3:4-dicarboxylphenylimide (LAWSON, PERKIN, and ROBINSON), 639.

$C_{14}H_{10}O_3N$ 6-Nitro-9-methylacridone (CLEMO, PERKIN, and ROBINSON), 1774.

$C_{14}H_{10}O_3N_2$ 9-Nitro-*N*-methylacridone (BURTON and GIBSON), 2503.

$C_{14}H_{10}O_3S$ Anthracene-1-sulphonic acid, aniline salt (BARNETT and MATTHEWS), 1082.

$C_{14}H_{10}O_4S$ Anthronesulphonic acids, and their salts (BARNETT and MATTHEWS), 1080.

$C_{14}H_{10}O_6S_2$ Anthracenedisulphonic acids, aniline salts (BARNETT and MATTHEWS), 1082.

$C_{14}H_{10}O_7S_2$ Anthronedisulphonic acids, and their salts (BARNETT and MATTHEWS), 1080.

$C_{14}H_{10}O_8S_2$ Salicylic acid 5-disulphoxide (BERE and SMILES), 2362.

$C_{14}H_{11}ON$ 1:3-Dimethylpyridofluorenone (MILLS, PALMER, and TOMKINSON), 2369.

$C_{14}H_{11}O_6N_3$ Methoxybenz*syn*aldoximes 2:4-dinitrophenyl ethers (BRADY and TRUSZKOWSKI), 1091.

$C_{14}H_{12}ON_2$ Anhydro-2'-amino-*N*-methyldiphenylamine-6-carboxylic acid (BURTON and GIBSON), 2503.

$C_{14}H_{12}O_2N_2$ Benzildioximes, isomeric (BRADY and DUNN), 291.

$C_{14}H_{12}O_2S_2$ 3-Carboxyphenyl-4-tolyl disulphide (SMILES and GIBSON), 182.

$C_{14}H_{12}O_3N_2$ *p*-Nitrobenz*syn*aldoxime *O*-benzyl ether (BRADY and MCHUGH), 553.

*p*-Nitrobenzophenoneoxime methyl ethers (BRADY and MEHTA), 2302.

$C_{14}H_{12}O_4N_2$ 2'-Nitro-*N*-methyldiphenylamine-6-carboxylic acid (BURTON and GIBSON), 2502.

$C_{14}H_{13}NCl$ 9-$\beta$-Chloroethylcarbazole (CLEMO and PERKIN), 1810.

$C_{14}H_{13}O_3As$ Benzophenone-*o*-methylarsinic acid (AESCHLIMANN and MCCLELAND), 2031.

$C_{14}H_{12}O_4N_2$ Dinitrodimethyldiphenylamines (BRADY, HEWETSON, and KLEIN), 2403.

$C_{14}H_{14}ON_2$ *N*-Hydroxyphenyl-*p*-tolylformamidines, and their salts (FARROW and INGOLD), 2546.

2-Phenyl-4-*p*-totylmethylene-1:2:4-oxadi-imine (INGOLD), 94.

$C_{14}H_{14}ON_4$ Benzylidene-5-anilinosemicarbazide (SUTHERLAND and WILSON), 2146.

$C_{14}H_{14}O_2N_2$ 2'-Amino-*N*-methyldiphenylamine-6-carboxylic acid (BURTON and GIBSON), 2502.

$C_{14}H_{14}O_3N_2$ Acetylketotetrahydronorharmine (NISHIKAWA, PERKIN, and ROBINSON), 661.

$C_{14}H_{14}O_6N_2$ α- and β-Diacetyltartarophenylhydrazides (CHATTAWAY and PARKES), 469.

$C_{14}H_{15}O_2N_3$ α-Naphthyl methoxymethyl ketone semicarbazone (RIDGWAY and ROBINSON), 219.

$C_{14}H_{15}O_3N_3$ 6-Cyanoindole-2-carboxydimethylacetalylamide (KERMACK), 2289.

$C_{14}H_{15}O_4N$ Ethyl indole-2:6-dicarboxylate (KERMACK), 2287.

$C_{14}H_{15}O_5N$ 5-Ethoxy-2-carboxy-1-methylindole-3-acetic acid (STEDMAN), 1376.

$C_{14}H_{15}O_7N$ Ethyl 2-nitro-4-carbethoxyphenylpyruvate (KERMACK), 2287.

$C_{14}H_{15}N_2Cl$ β-*o*-Chlorophenylaminoethylaniline, and its hydrochloride (CLEMO and PERKIN), 1809.

$C_{14}H_{16}O_2N_2$ *o*-Dianisidine, hydroferrocyanide of (CUMMING), 2541.

*N*-Hydroxyphenyl-*p*-tolylformamidine hydrates (FARROW and INGOLD), 2547.

$C_{14}H_{16}O_7N_2$ Diacetyltartarophenylhydrazido-acid (CHATTAWAY and PARKES), 469.

$C_{14}H_{16}NCl$ 9-β-Chloroethyltetrahydrocarbazole (CLEMO and PERKIN), 1813.

$C_{14}H_{17}ON$ 9-β-Hydroxyethyltetrahydrocarbazole (CLEMO and PERKIN), 1811.

$C_{14}H_{17}ON_3$ Styryl *iso*butenyl ketone semicarbazone (WILSON and MACAULAY), 843.

$C_{14}H_{17}O_2N$ 3-Methyl*cyclo*hexylideneanthranilic acid (PERKIN and SEDGWICK), 2442.

Octahydroacridinecarboxylic acids (PERKIN and SEDGWICK), 2450.

$C_{14}H_{17}O_2N_3$ Benzylidene derivative of piperidinooxalylhydrazine (WILSON and PICKERING), 1155.

$C_{14}H_{17}O_5N$ Ethyl 2-phenyldimethylene-1:2-oxaimine-4:4-dicarboxylate (INGOLD and WEAVER), 1459.

$C_{14}H_{18}O_4N_2$ 5-Methoxyindole-2-carboxydimethylacetalylamide (BLAIKIE and PERKIN), 318.

$C_{14}H_{18}O_8N_2$ Phenylhydrazine diacetyltartrate (CHATTAWAY and PARKES), 468.

$C_{14}H_{19}ON$ 9-Acetyloctahydrocarbazole (PERKIN and PLANT), 1508.

$C_{14}H_{20}NI$ Octahydroacridine methiodide (PERKIN and SEDGWICK), 2450.

$C_{14}H_{22}NI$ 9-Methyloctahydrocarbazole methiodide (PERKIN and PLANT), 1510.

## 14 IV

$C_{14}H_9O_4BrS$ 10-Bromo-9-hydroxyphenanthrene-2-sulphonic acid, and its salts (HENSTOCK), 1298.

$C_{14}H_9O_5NS$ Nitroanthracenesulphonic acids (BARNETT and MATTHEWS), 1082.

$C_{14}H_{10}ONI$ 3-Iodo-*N*-acetylcarbazole (TUCKER), 1148.

$C_{14}H_{12}O_2NBr$ α-Bromo-β-phenylpropionic acid-β-pyridinium betaine (BARNETT, COOK, and PECK), 1039.

$C_{14}H_{12}O_3NAs$ *N*-Acetylphenarsazinic acid (BURTON and GIBSON), 2277.

$C_{14}H_{12}N_2Cl_2S$ 2:4-Dichlorophenyl-*p*-tolylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{14}H_{13}ON_2Cl$ *p*-Chlorophenyl-*p*-tolylcarbamide (INGOLD), 99.

4-*p*-Chlorophenyl-2-*p*-tolylmethylene-1:2:4-oxadi-imine (INGOLD), 95.

$C_{14}H_{13}ONBr_2$ α-Bromo-β-phenylpropionic acid-β-pyridinium bromide (BARNETT, COOK, and PECK), 1039.

$C_{14}H_{13}ON_2Br$ *p*-Bromophenyl-*p*-tolylcarbamide (INGOLD), 100.

4-*p*-Bromophenyl-2-*p*-tolylmethylene-1:2:4-oxadi-imine (INGOLD), 95.

$C_{14}H_{13}O_2N_2Cl$ 9-Chloro-12-methoxy-5-keto-4:7-dimethyl-4:5-dihydroindolediazine-(1:4) (BLAIKIE and PERKIN), 322.

$C_{14}H_{13}N_2ClS$ þ-Chlorophenyltolylthiocarbamides (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{14}H_{13}N_2BrS$ *p*-Bromophenyl-*p*-tolylthiocarbamide (CHATTAWAY, HARDY, and WATTS), 1555.

$C_{14}H_{14}N_4Cl_6Pb$ *o*-Toluenediazonium plumbichloride (CHATTAWAY, GARTON, and PARKES), 1985.

$C_{14}H_{16}O_4N_2S$ 5-Methyl-5-*iso*carboline methosulphate (ROBINSON and THORNLEY), 2173.

$C_{14}H_{16}O_5NCl$ Ethyl 2-*p*-chlorophenyldimethylene-1:2-oxaimine-4:4-dicarboxylate (INGOLD and WEAVER), 1460.

$C_{14}H_{16}O_5NBr$ Ethyl 2-*p*-bromophenyldimethylene-1:2-oxaimine-4:4-dicarboxylate (INGOLD and WEAVER), 1461.

$C_{14}H_{18}NCl_4I$ Dibenzylammonium tetrachloroiodide (CHATTAWAY and GARTON), 188.

$C_{14}H_{18}O_4Cl_6Te$ Dimethylpyrone tellurichloride (MORGAN and DREW), 757.

$C_{14}H_{18}O_5Cl_4Te$ Dimethylpyrone tellurioxychloride (MORGAN and DREW), 751.

$C_{14}H_{22}O_4Br_2Sn$ Stannic bis-3-ethylacetylacetone dibromide (MORGAN and DREW), 380.

## 14 V

$C_{14}H_{11}ONClAs$ 10-Chloro-5-acetyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 2277.

$C_{14}H_{11}O_7N_2ClS$ 6-Chloro-2:4-dinitro-*m*-tolyl *p*-toluenesulphonate (SANÉ and JOSHI), 2483.

$C_{14}H_{13}O_4N_2ClS$ Toluene-*p*-sulphonyl-6-chloro-5-nitro-*o*-toluidide (MORGAN and GLOVER), 1599.

$C_{14}H_{14}O_2NClS$ Toluene-*p*-sulphonyl-6-chloro-*o*-toluidide (MORGAN and GLOVER), 1599.

# $C_{15}$ Group.

$C_{15}H_{24}$ *n*- and *iso*-Cadinene (HENDERSON and ROBERTSON), 1992.

## 15 II

$C_{15}H_{10}N_2$ 3:4-Quinindoline, and its salts (CLEMO and PERKIN), 1618.

$C_{15}H_{10}N_4$ 1-α-Quinolylbenzotriazole (LAWSON, PERKIN, and ROBINSON), 634.

$C_{15}H_{13}N_3$ Phenylpyruvonitrilephenylhydrazone (WALKER), 1623.

$C_{15}H_{14}O$ Methyldeoxybenzoin, preparation of (MCKENZIE and ROGER), 850.

$C_{15}H_{14}N$ 11:12-Dihydroacridoxaline (CLEMO, PERKIN, and ROBINSON), 1790.

$C_{15}H_{14}N_2$ 9-Ethylaminoacridine (CLEMO, PERKIN, and ROBINSON), 1787.

$C_{15}H_{15}N_3$ 4-Tetrahydroquinolonephenylhydrazone (CLEMO and PERKIN), 1618.

$C_{15}H_{16}O_2$ Methylhydrobenzoins, optically active, dehydration of (MCKENZIE and ROGER), 2148.

$C_{15}H_{18}N_2$ *dl*-Diphenylpropylenediamine, resolution of (KIPPING and POPE), 2396.

$C_{15}H_{20}O_4$ Ethyl β-phenylglutarate (SPEIGHT, STEVENSON, and THORPE), 2190.

$C_{15}H_{26}O$ Cadinol (HENDERSON and ROBERTSON), 1995.

$C_{15}H_{22}O_2$ Cadinene glycol (HENDERSON and ROBERTSON), 1994.

## 15 III

$C_{15}H_7O_7N$ Pyridofluorenone-1:3:4-tricarboxylic acid (MILLS, PALMER, and TOMKINSON), 2368.

$C_{15}H_9O_6N$ Pyridofluorene-1:3:4-tricarboxylic acid (MILLS, PALMER, and TOMKINSON), 2369.

$C_{15}H_{10}O_2S$ 2-Benzoyl-3-oxy(1)thionaphthen (HART and SMILES), 880.

$C_{15}H_{11}O_2N_3$ Nitrosoanhydrodihydroacridine-9-aminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1789.

$C_{15}H_{11}O_3N$ 1:3-Dimethylpyridofluorene-4-carboxylic acid (MILLS, PALMER, and TOMKINSON), 2368.

$C_{15}H_{11}O_3Cl$ 3:7-Dihydroxy-2-phenylbenzopyrylium chloride (+ $H_2O$) (PRATT and ROBINSON), 192.

$C_{15}H_{11}O_4Cl$ 3:7:4′-Trihydroxy-2-phenylbenzopyrylium chloride (+ $H_2O$) (PRATT and ROBINSON), 192.

$C_{15}H_{11}O_5Cl$ Pelargonidin chloride (+ $H_2O$) (PRATT and ROBINSON), 198.

$C_{15}H_{11}N_2Br$ 2-Bromo-4:5-diphenylglyoxaline, and its salts (LAMB and PYMAN), 709.

$C_{15}H_{12}ON_2$ 9-Acetylaminoacridine (CLEMO, PERKIN, and ROBINSON), 1785.

Anhydrodihydroacridine-9-aminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1788.

$C_{15}H_{12}O_2N_2$ Acridine-9-aminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1786.

Anhydro-2′-acetylaminodiphenylamine-6-carboxylic acid (CLEMO, PERKIN, and ROBINSON), 1779.

$C_{15}H_{12}O_2N_4$ Phenylpyruvonitrile-*p*-nitrophenylhydrazone (WALKER), 1624.

$C_{15}H_{12}O_3Br_2$ 3:3′-Dibromoditolyl carbonate (GRIFFITH), 2627.

$C_{15}H_{12}O_4N_2$ Acetyl-*anti*-*p*-nitrobenzophenoneoxime (BRADY and MEHTA), 2303.

$C_{15}H_{12}N_3Cl$ 5-Chloro-4-phenyl-1-*p*-tolyl-1:2:3-triazole (CARNELLEY and DUTT), 2478.

$C_{15}H_{13}ON_3$ 5-Hydroxy-4-phenyl-1-*p*-tolyl-1:2:3-triazole (CARNELLEY and DUTT), 2478.

$C_{15}H_{13}O_5N_3$ Carbanilino-3-nitro-*p*-methoxybenzaldoximes (BRADY and MANJUNATH), 1063.

$C_{15}H_{13}O_7N_3$ 3:4-Dimethoxybenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1092.

$C_{15}H_{12}O_7N_5$ 3-Nitro-*p*-dimethylaminobenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.

$C_{15}H_{14}ON_2$ 9-Acetylamino-5:10-dihydroacridine (CLEMO, PERKIN, and ROBINSON), 1785.

Anhydro-2′-amino-*N*-ethyldiphenylamine-6-carboxylic acid (BURTON and GIBSON), 2504.

9-β-Hydroxyethylaminoacridine (CLEMO, PERKIN, and ROBINSON), 1792.

$C_{15}H_{14}O_4N_2$ 6-Carboxydiphenylamine-2′-aminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1782.

2′-Nitro-*N*-ethyldiphenylamine-6-carboxylic acid (BURTON and GIBSON), 2504.

$C_{15}H_{14}O_5N$ *p*-Dimethylaminobenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.

$C_{15}H_{15}ON$ Tetrahydrocarbazole-9:8-anhydropropionic acid (CLEMO and PERKIN), 1619.

$C_{15}H_{15}O_2N$ Benzo-β-hydroxyethylanilide (CLEMO and PERKIN), 1810.

$C_{15}H_{15}O_4N_3$ Nitro-2:3-dimethoxybenzylideneanilines, and their hydrochlorides (PERKIN, ROBINSON, and STOYLE), 2357.

$C_{15}H_{16}ON_2$ Acetylaminotetrahydroacridine (PERKIN and SEDGWICK), 2447.

9-β-Hydroxyethylaminodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1793.

$C_{15}H_{16}ON_4$ Acetophenone-δ-anilinosemicarbazone (SUTHERLAND and WILSON), 2146.

$C_{15}H_{16}O_2N_2$ Acetylaminotetrahydroacridones (PERKIN and SEDGWICK), 2445.

2′-Amino-*N*-ethyldiphenylamine-6-carboxylic acid, and its silver salt (BURTON and GIBSON), 2504.

$C_{15}H_{16}N_6S_3$ Thiocarbohydrazidedicarbonthiophenylamide (GUHA and DE), 1217.

$C_{15}H_{17}ON_3$ Cyanomethyltetrahydroharmine (NISHIKAWA, PERKIN, and ROBINSON), 660.

$C_{15}H_{18}ON_2$ 1-*cyclo*Hexylideneamino-4-tetrahydroquinolone (CLEMO and PERKIN), 1619.

$C_{15}H_{19}ON$ Acetyloctahydroacridine (PERKIN and SEDGWICK), 2449.
$C_{15}H_{19}O_2N$ Benzoylvinyldiacetonamines, isomeric (KIPPING and GREASLEY), 2614.
$C_{15}H_{19}O_2N_3$ Acetophenone piperidinooxalylhydrazone (WILSON and PICKERING), 1155.
1-*p*-Nitrophenyl-3:5-di-*n*-propylpyrazole (MORGAN and THOMASON), 756.
$C_{15}H_{20}ON_2$ Acetylamino-octahydroacridine (PERKIN and SEDGWICK), 2447.
$C_{15}H_{20}O_4N_2$ Methoxyindole-2-carboxydimethylacetalylmethylamides (BLAIKIE and PERKIN), 316.
$C_{15}H_{21}O_2N$ β-Eucaines, salts of (KING), 48.
$C_{15}H_{21}O_2N_3$ Eserine (STEDMAN), 1373.
$C_{15}H_{22}O_2N_6$ Styryl *iso*butenyl ketone semicarbazide-semicarbazone (WILSON and MACAULAY), 844.

## 15 IV

$C_{15}H_{10}O_7N_2Br_2$ Dibromodinitroditolyl carbonate (GRIFFITH), 2627.
$C_{15}H_{12}O_3N_2S$ 4:5-Diphenylglyoxaline-2-sulphonic acid, salts (LAMB and PYMAN), 709.
$C_{15}H_{12}O_7N_3Br$ 5-Bromo-3:4-dimethoxybenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1091.
$C_{15}H_{13}O_3N_2Br$ Carbanilino-3-bromo-*p*-methoxybenzaldoximes (BRADY and MANJUNATH), 1065.
$C_{15}H_{13}O_5N_4Br$ 3-Bromo-*p*-dimethylaminobenz*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and TRUSZKOWSKI), 1092.
$C_{15}H_{14}O_2NBr$ 3-Bromo-*p*-methoxybenzaldoxime benzyl ethers (BRADY and MANJUNATH), 1064.
$C_{15}H_{14}O_3NAs$ *N*-Propionylphenarsazinic acid (BURTON and GIBSON), 2277.
$C_{15}H_{15}ONBr_2$ Bromodihydrosafrolepyridinium bromide (BARNETT, COOK, and PECK), 1038.
$C_{15}H_{15}O_2NBr_2$ Methyl α-bromo-β-phenylpropionate-β-pyridinium bromide (BARNETT, COOK, and PECK), 1039.
$C_{15}H_{15}O_2NS$ Toluene-*p*-sulphonvinylanilide (CLEMO and PERKIN), 1808.
$C_{15}H_{16}ON_6S_2$ Carbohydrazidedicarbonthiophenylamide (GUHA and DE), 1217.
$C_{15}H_{17}ONBr_2$ Bromodihydroanetholepyridinium bromide (BARNETT, COOK, and PECK), 1037.
$C_{15}H_{21}O_6ClZr$ Zirconium trisacetylacetone chloride (MORGAN and BOWEN), 1258.

## 15 V

$C_{15}H_{13}ONClAs$ 10-Chloro-5-propionyl-5:10-dihydrophenarsazine (BURTON and GIBSON), 2277.
$C_{15}H_{16}O_2NClS$ Toluene-*p*-sulphon-β-chloroethylanilide (CLEMO and PERKIN), 1808.
$C_{15}H_{21}O_6Cl_2CuGe$ Germanium trisacetylacetone cuprochloride (MORGAN and DREW), 1267.
$C_{15}H_{21}O_6Br_2CuGe$ Germanium trisacetylacetone cuprobromide (MORGAN and DREW), 1268.
$C_{15}H_{21}O_6Br_3CuGe$ Germanium trisacetylacetone cupribromide (MORGAN and DREW), 1268.
$C_{15}H_{21}O_6Br_3Cu_2Ge$ Germanium trisacetylacetone dicuprobromide (MORGAN and DREW), 1268.

# $C_{16}$ Group.

$C_{16}H_{10}N_2$ 2:3-Quinoquinoline (CLEMO and PERKIN), 1620.
$C_{16}H_{12}O_4$ 7-Hydroxy-3-methoxyflavone (ALLAN and ROBINSON), 2194.
$C_{16}H_{12}O_5$ Succinylfluorescein (DUTT and THORPE), 2530.

$C_{16}H_{12}N_2$ Dihydro-2:3-quinoquinoline (CLEMO and PERKIN), 1620.

$C_{16}H_{12}N_6$ 1:1′-(4:4′-Diphenylyl)-bis-1:2:3-triazole (CHATTAWAY, GARTON, and PARKES), 1988.

$C_{16}H_{12}S_2$ Phenyl-2-naphthyl disulphide (SMILES and GIBSON), 182.

$C_{16}H_{14}O_2$ 2-Methoxystyryl phenyl ketone (FORSTER and HEILBRON), 345.

$C_{16}H_{14}O_3$ 2-Hydroxy-3-methoxystyryl phenyl ketone (ROBINSON and ROBERTS), 208.

$C_{16}H_{14}O_5$ *o*- and *m*-Methoxybenzoic anhydrides (RULE and PATERSON), 2161.

$C_{16}H_{15}N_3$ Phenylpyruvonitrile-*p*-tolylhydrazone (WALKER), 1624.

$C_{16}H_{16}N_2$ 3-Methylbenzo-(5:6)-9:10:11:12-tetrahydro-4-carboline (G. M. and R. ROBINSON), 837.

$C_{16}H_{18}O_2$ Ethylhydrobenzoins, optically active, dehydration of (MCKENZIE and ROGER), 2148.

$C_{16}H_{22}N_2$ 1:4:4:6:6-Pentamethyl-3:4:5:6-tetrahydro-5-carboline (ROBINSON and THORNLEY), 2175.

$C_{16}H_{24}O_7$ Ethyl 2-acetyl*cyclo*pentane-1:2:3-tricarboxylate (BERNTON, ING, and PERKIN), 1498.

$C_{16}H_{26}O_9$ Tetramethyl dimannose (IRVINE and BURT), 1348.

$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, hydration of curd fibres of (BENNETT), 1971; thallous salt (MENZIES and WILKINS), 1149.

## 16 III

$C_{16}H_{12}O_3N_2$ 6-Anilino-2:4-diketo-3-phenyl-2:4-dihydro-1:3-oxazine (INGOLD and WEAVER), 1460.

$C_{16}H_{13}ON$ 3-Benzylidene-4-tetrahydroquinolone (CLEMO and PERKIN), 1617.

$C_{16}H_{13}O_2N$ Benzoyl-4-tetrahydroquinolone (CLEMO and PERKIN), 1617.

$C_{16}H_{13}O_2N_3$ Benzil semioxamazone (WILSON and PICKERING), 1153.

$C_{16}H_{13}O_3Cl$ 7-Hydroxy-4′-methoxy-2-phenylbenzopyrylium chloride (PRATT, ROBINSON, and WILLIAMS), 203.

$C_{16}H_{13}O_4N$ Styrylmethylpyridinedicarboxylic acid, and its salts (LAWSON, PERKIN, and ROBINSON), 637.

$C_{16}H_{13}O_4N_3$ Nitroso-derivative of methyl acridone-9-aminoacetate (CLEMO, PERKIN, and ROBINSON), 1776.

$C_{16}H_{13}O_4Cl$ Acacetidin chloride (PRATT, ROBINSON, and WILLIAMS), 204.

$C_{16}H_{13}O_6N_3$ *o*-Methoxycinnam*syn*aldoxime 2:4-dinitrophenyl ether (BRADY and GRAYSON), 1420.

$C_{16}H_{14}ON_2$ Anhydro-5:10-dihydroacridine-9-methylaminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1797.

$C_{16}H_{14}O_3N_2$ Methyl acridone-9-aminoacetate (CLEMO, PERKIN, and ROBINSON), 1776.

$C_{16}H_{16}O_2N$ Anilo-4-carboxy-2:6-dimethylbenzaldehyde (PERKIN and TAPLEY), 2435.

2-Carboxy-2:6-dimethylbenzaldehyde anilide (PERKIN and TAPLEY), 2436.

$C_{16}H_{16}O_5N_2$ Methoxyphenylpyruvic acid phenylhydrazones (BLAIKIE and PERKIN), 308.

$C_{16}H_{16}O_3N_2$ 4-Carboxy-2:6-dimethylbenzaldehyde phenylhydrazone (PERKIN and TAPLEY), 2435.

$C_{16}H_{16}O_3N_2$ 2′-Acetylamino-*N*-methyldiphenylamine-6-carboxylic acid, and its silver salt (BURTON and GIBSON), 2503.

$C_{16}H_{16}O_3N_4$ Mesoxmono-*p*-tolylamide phenylhydrazone (PLOWMAN and WHITELEY), 602.

$C_{16}H_{16}N_4S_2$ Dithio-*p*-urazine dibenzyl ether (GUHA and DE), 1217.

$C_{16}H_{17}ON_3$ Methyldeoxybenzoin semicarbazone (MCKENZIE and ROGER), 850.

$C_{16}H_{17}O_3N_3$ 4-Methoxy-2-aldehydophenylglycine phenylhydrazone (BLAIKIE and PERKIN), 326.

$C_{16}H_{17}O_4N_3$ Nitro-2:3-dimethoxybenzylidene-*p*-toluidines (PERKIN, ROBINSON, and STOYLE), 2357.

$C_{16}H_{18}O_3N_4$ Mesoxmono-*p*-tolylamide phenylhydrazone hydrate (PLOWMAN and WHITELEY), 602.

$C_{16}H_{19}O_2N_3$ *cyclo*Hexanonequinaldyl-3-hydrazone dioxide (G. M. and R. ROBINSON), 834.

$C_{16}H_{22}O_4N_2$ 5-Methoxyindole-2-carboxyacetalylamide (BLAIKIE and PERKIN), 318.

$C_{16}H_{34}O_3S$ Di-*d*-β-octyl sulphite (HUNTER), 1395.

## 16 IV

$C_{16}H_{10}O_2N_2S$ 2-Thionaphthen-2-quinoxalineindigotin (HART and SMILES), 880.

$C_{16}H_{10}O_3NBr_2$ 8-Bromo-6-benzoylaminocoumarin (DEY and ROW), 561.

$C_{16}H_{10}O_9N_4Na_2$ Tartrazine, estimation of, volumetrically (KNECHT), 1544.

$C_{16}H_{11}ON_4Cl_3$ 1-*m*-Chlorophenyl-3-methyl-5-pyrazolone-4-azo-2′:4′-dichlorobenzene (CHATTAWAY and STROUTS), 2425.

$C_{16}H_{11}O_2N_2Cl_3$ Chlorofumarodi-*p*-chloroanilide (CHATTAWAY and PARKES), 466.

$C_{16}H_{11}O_3NS$ Anil of 3-oxy(1)-thionaphthen-2-glyoxylic acid (HART and SMILES), 880.

$C_{16}H_{12}ON_4Cl_2$ 1-*o*- and -*p*-Chlorophenyl-3-methyl-5-pyrazolone-4-azo-*o*- and -*p*-chlorobenzenes (CHATTAWAY and STROUTS), 2426.

1-2:4-Dichlorophenyl-3-methyl-5-pyrazolone-4-azobenzene (CHATTAWAY and STROUTS), 2427.

$C_{16}H_{12}O_3N_2S$ *o*-Aminoanil of 3-oxy(1)thionaphthen-2-glyoxylic acid (HART and SMILES), 880.

3-Oxy(1)thionaphthen-2-glyoxylic acid. phenylhydrazone (HART and SMILES), 880.

$C_{16}H_{13}ON_2Cl_3$ 1-Chlorophenyl-3-methyl-4-benzylidene-5-pyrazolones (CHATTAWAY and STROUTS), 2424.

$C_{16}H_{13}O_6Cl_4Fe$ 8-Methoxy-2-phenylbenzopyrylium ferrichloride (ROBINSON and ROBERTS), 209.

$C_{16}H_{13}O_4N_2I$ Methyltetrahydroxydibenzoharmyrine hydriodide (LAWSON, PERKIN, and ROBINSON), 645.

$C_{16}H_{14}O_4ClAs$ *oo′*-Dicarbomethoxydiphenylchloroarsine (AESCHLIMANN and MCCLELAND), 2035.

$C_{16}H_{15}O_3SN$ *N*-Toluene-*p*-sulphonyltetrahydroquinolone (CLEMO and PERKIN), 1616.

$C_{16}H_{16}O_4N_2S_2$ Acetanilide-*p*-disulphoxide (BERE and SMILES), 2361.

$C_{16}H_{17}O_2NBr_2$ Ethyl α-bromo-β-phenylpropionate-β-pyridinium bromide (BARNETT, COOK, and PECK), 1039.

$C_{16}H_{17}O_4NS$ Toluene-*p*-sulphonyl-β-anilinopropionic acid (CLEMO and PERKIN), 1614.

$C_{16}H_{17}O_6N_2As$ *p′*-Carbethoxyaminobenzoyl-*p*-aminophenylarsinic acid (KING and MURCH), 2603.

$C_{16}H_{26}O_4Cl_2Te$ Tellurium bis*iso*valerylacetone dichloride (MORGAN and DREW), 744.

$C_{16}H_{32}O_4Cl_6Te$ Dimethyldihydroresorcinol tellurichloride (MORGAN and DREW), 752.

## 16 V

$C_{16}H_8O_2N_2ClBr_3$ Chlorofumarodi-*p*-bromoanilide (CHATTAWAY and PARKES), 467.

$C_{16}H_{14}O_3NClS$ *N*-Toluene-*p*-sulphonyl-3-chlorotetrahydroquinolone (CLEMO and PERKIN), 1616.

## $C_{17}$ Group.

$C_{17}H_{16}O_3$ 2′-Hydroxy-3′-methoxy-2-benzylidene-1-hydrindone (Robinson and Lawson), 213.

$C_{17}H_{14}O_5$ Glutarylfluorescein (Dutt and Thorpe), 2531.

$C_{17}H_{15}N_3$ Benzaldehydequinaldyl-3-hydrazone, and its hydrochloride (G. M. and R. Robinson), 834.

$C_{17}H_{16}O_3$ 2-Hydroxy-5-methylstyryl 4-methoxyphenyl ketone (Robinson and Hunt), 208.

$C_{17}H_{16}O_6$ 2′-Hydroxy-3:4-dimethoxymethyl-2-benzoylbenzoic acids (Simonsen), 722.

$C_{17}H_{17}O_3$ Di-*d*-β-octyl carbonate, rotatory power of (Hunter), 1394.

$C_{17}H_{15}N_2$ 3:4-Dimethylbenzo-(5:6)-9:10:11:12-tetrahydro-4-*iso*carboline (G. M. and R. Robinson), 838.

$C_{17}H_{20}O$ Benzylidenecamphor, absorption spectra of (Lowry and French), 1921.

$C_{17}H_{20}O_4$ Ethyl 3-*o*-methoxyphenyl-5-methyl-$\Delta^5$-*cyclo*hexen-1-one-2- or -4-carboxylate (Forster and Heilbron), 344.

$C_{17}H_{20}N_2$ 1:4-Diphenyl-2-methylpiperazines, and the *d*-camphor-β-sulphonate of the *l*-form (Kipping and Pope), 2396.

$C_{17}H_{24}O$ 2- and 6-Benzyl-*dl-iso*menthones (Read, Smith, and Hughesdon), 134.

$C_{17}H_{36}O_2$ Di-*d*-β-octylformal, rotatory power of (Hunter), 1393.

### 17 III

$C_{17}H_{10}O_5I_4$ Tetraiododiacetyldihydroxybenzophenone (Spiers), 1458.

$C_{17}H_{11}O_4Cl$ *o*-Chlorobenzoyl derivative of 7-hydroxy-4-methylcoumarin (Barger and Eaton), 2410.

$C_{17}H_{11}O_6N$ Nitrobenzoyl derivatives of 7-hydroxy-4-methylcoumarin (Barger and Eaton), 2410.

$C_{17}H_{12}O_3S$ 2-Acetyl-3-benzoyloxy(1)thionaphthen (Hart and Smiles), 881.

2-Benzoyl-3-acetoxy(1)thionaphthen (Hart and Smiles), 881.

$C_{17}H_{13}O_4N$ Phenylcarbimido-derivative of 7-hydroxy-4-methylcoumarin (Barger and Eaton), 2410.

*d*- and *l*-β-Phthalimino-β-phenylpropionic acids (McKenzie and Tudhope), 926

$C_{17}H_{13}O_4N_3$ Dinitro-3-methylphenylnaphthylamines (Brady, Hewetson, and Klein), 2403.

$C_{17}H_{14}O_2N_2$ Acetylanhydroacridine-9-aminoacetic acid (Clemo, Perkin, and Robinson), 1789.

$C_{17}H_{14}O_3N_2$ Anhydro-5:10-dihydroacridine-9-aminodiacetic acid (Clemo, Perkin, and Robinson), 1797.

$C_{17}H_{14}O_5N_2$ *N-o*-Nitrobenzoylnorhydrohydrastinine (Haworth, Perkin, and Rankin), 1700.

$C_{17}H_{15}O_3N$ Benzoyl-*o*-methoxycinnam*anti*aldoxime (Brady and Grayson), 1419.

$C_{17}H_{15}O_2N_3$ Nitroso-derivative of ethyl acridine-9-aminoacetate (Clemo, Perkin, and Robinson), 1786.

$C_{17}H_{15}O_4N$ Anilodimethylterephthalonic acid, aniline salt (Perkin and Tapley), 2435.

$C_{17}H_{15}O_4N_3$ Nitroso-derivative of ethyl acridone-9-aminoacetate (Clemo, Perkin, and Robinson), 1777.

Nitroso-derivative of ethyl anhydro-6-carboxydiphenylamine-2′-aminoacetate (Clemo, Perkin, and Robinson), 1782.

$C_{17}H_{16}ON_2$ Acetyl-11:12-dihydroacridoxaline (CLEMO, PERKIN, and ROBINSON), 1790.

9-Acetylethylaminoacridine (CLEMO, PERKIN, and ROBINSON), 1787.

$C_{17}H_{16}O_2N_2$ Ethyl acridine-9-aminoacetate (CLEMO, PERKIN, and ROBINSON), 1786.

$C_{17}H_{16}O_3N_2$ Ethyl acridone-9-aminoacetate (CLEMO, PERKIN, and ROBINSON), 1776.

Ethyl anhydro-6-carboxydiphenylamine-2′-aminoacetate (CLEMO, PERKIN, and ROBINSON), 1782.

$C_{17}H_{16}O_3N_2$ Mesox-*p*-toluidide (PLOWMAN and WHITELEY), 597.

$C_{17}H_{16}O_4N_2$ Dimethylterephthalonic acid phenylhydrazone (PERKIN and TAPLEY), 2433.

$C_{17}H_{16}O_4N_2$ Ethyl 6-carboxy-2′-nitrodiphenylamine-*N*-acetate (LINNELL and PERKIN), 2456.

$C_{17}H_{16}O_5N_2$ Dinitroveratrone (LAWSON, PERKIN, and ROBINSON), 640.

$C_{17}H_{17}ON_3$ Dypnone semicarbazones (WILSON and MACAULAY), 841.

$C_{17}H_{17}O_2N_3$ Dibenzyl ketone semioxamazone (WILSON and PICKERING), 1153.

$C_{25}H_{17}O_3N$ β-Phthalimino-β-phenylpropiophenones, optically active (MCKENZIE and TUDHOPE), 923.

$C_{17}H_{18}O_2N_2$ 9-Aminoacridine dimethylacetal (CLEMO, PERKIN, and ROBINSON), 1795.

Acetyl derivative of 9-β-hydroxyethylaminodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1794.

$C_{17}H_{18}O_3N_2$ 2′-Acetylamino-*N*-ethyldiphenylamine-6-carboxylic acid, and its silver salt (BURTON and GIBSON), 2504.

$C_{17}H_{18}O_4N_2$ Dihydroxymesox-*p*-toluidide (PLOWMAN and WHITELEY), 597.

$C_{17}H_{19}O_4N_3$ *iso*Nitrosomalon-*p*-toluidide (PLOWMAN and WHITELEY), 597.

$C_{17}H_{20}O_2N_2$ 9-Amino-5:10-dihydroacridine dimethylacetal (CLEMO, PERKIN, and ROBINSON), 1795.

$C_{17}H_{20}O_4N_2$ *d*-Camphor-*o*- and -*m*-nitrobenzylimides (SINGH and BISWAS), 1896.

$C_{17}H_{20}O_5N_2$ Diaminoveratrone (LAWSON, PERKIN, and ROBINSON), 641.

$C_{17}H_{20}N_6S_3$ Thiocarbohydrazidedicarbonthio-*p*-tolylamide (GUHA and DE), 1217.

$C_{17}H_{21}O_3N$ *d*-Camphorbenzylimide, rotatory dispersion of (SINGH and BISWAS), 1895.

$C_{17}H_{23}ON_2$ Tetramethyldiaminobenzhydrol, and its volumetric estimation (KNECHT), 1541.

$C_{17}H_{22}O_5N_2$ *p*-Nitrobenzyl-*d*-camphoramic acids (SINGH and BISWAS), 1897.

$C_{17}H_{23}OCl$ 2-Benzylidene-*dl*-*iso*menthone hydrochlorides (READ, SMITH, and HUGHESDON), 133.

$C_{17}H_{23}O_3N$ Benzyl-*d*-camphoramic acid, rotatory dispersion of (SINGH and BISWAS), 1895.

$C_{17}H_{24}O_4N_2$ 5-Methoxyindole-2-carboxyacetalylmethylamide (BLAIKIE and PERKIN), 318.

$C_{17}H_{25}ON_3$ Acetyltriacetonamine phenylhydrazone (ROBINSON and THORNLEY), 2174.

## 17 IV

$C_{17}H_{12}ON_2Cl_2$ 1-2:4-Dichlorophenyl-3-methyl-4-benzylidene-5-pyrazolone (CHATTAWAY and STROUTS), 2427.

$C_{17}H_{13}O_2Cl_4Fe$ 8-Methoxy-2:3-indeno(1:2)benzopyrylium ferrichloride (ROBINSON and LAWSON), 213.

$C_{17}H_{15}OCl_4Fe$ 2-Phenyl-3:4′-dimethylbenzopyrylium ferrichloride (ROBINSON and DAS), 211.

$C_{17}H_{15}O_2Cl_4Fe$ 8-Ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 216.

4′-Methoxy-2-phenyl-6-methylbenzopyrylium ferrichloride (ROBINSON and LUNT), 208.

$C_{17}H_{15}O_3Cl_4Fe$ 6:4′-Dimethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 221.

8:4′-Dimethoxy-2-phenylbenzopyrylium ferrichloride (ROBINSON and WILLIAMS), 209.

Dimethylchrysinidin ferrichloride (PRATT, ROBINSON, and WILLIAMS), 201.

$C_{17}H_{16}O_6NCl$ 2:4-Diacetoxy-2′:4′-dihydroxybenzophenoneimine hydrochloride (SHOESMITH and HALDANE), 114.

$C_{17}H_{19}O_4NS$ Methyl toluene-*p*-sulphonyl-β-anilinopropionate (CLEMO and PERKIN), 1615.

$C_{17}H_{20}ON_6S_2$ Carbohydrazidedicarbonthio-*p*-tolylamide (GUHA and DE), 1217.

## $C_{18}$ Group.

$C_{18}H_{12}O_3$ 1-Benzoylnaphthalene-8-carboxylic acid (MASON), 2119.

$C_{18}H_{12}N_2$ 4:4′-Diquinolyl (CLEMO and PERKIN), 1622.

$C_{18}H_{13}N_3$ 2:2′-Diquinolylamine, and its salts (HAMER), 1353.

$C_{18}H_{14}O_4$ Phenylacetyl derivative of 7-hydroxy-4-methylcoumarin (BARGER and EATON), 2410.

$C_{18}H_{14}N_2$ 1:2-Dihydro-4:4′-diquinolyl (CLEMO and PERKIN), 1622.

$C_{18}H_{14}N_4$ 3:4-Diamino-7:12-dihydroacenaphthaphenazine (SIRCAR and GUHA), 339.

$C_{18}H_{16}O_5$ *as*-Dimethylsuccinylfluorescein (DUTT and THORPE), 2530.

1:2:8-Trimethoxymethylanthraquinones (SIMONSEN), 724.

$C_{18}H_{16}N_2$ *s*-Diphenyl-*o*-phenylenediamine (CLEMO, PERKIN, and ROBINSON), 1781.

1:2:1′:2′-Tetrahydro-4:4′-diquinolyl (CLEMO and PERKIN), 1621.

$C_{18}H_{17}N$ 9-Phenyltetrahydrocarbazole (LINNELL and PERKIN), 2459.

$C_{18}H_{18}O_6$ 2′:3:4-Trimethoxymethyl-2-benzoylbenzoic acids (SIMONSEN), 723.

$C_{18}H_{28}O_{14}$ Tetracarbethoxy fructose (ALLPRESS and HAWORTH), 1229.

$C_{18}H_{34}O_2$ Oleic acid, potassium salt, electrolysis of (HOLROYD and RHODES), 438; thallous salt (MENZIES and WILKINS), 1150.

$C_{18}H_{34}O_4$ Di-*l*-octyl oxalate, rotatory power of (LOWRY and RICHARDS), 1596.

$C_{18}H_{36}O_3$ γ-Hydroxystearic acid (CLUTTERBUCK), 2330.

### 18 III

$C_{18}H_6O_4N_4$ 3:4-Dinitroacenaphthaphenazine (SIRCAR and GUHA), 338.

$C_{18}H_{11}O_2Cl$ 1:8-Benzoylnaphthoyl chloride (MASON), 2121.

$C_{18}H_{12}O_2N_2$ 3:4-Dihydroxy-7:12-dihydroacenaphthaphenazine (SIRCAR and GUHA), 340.

$C_{18}H_{12}O_7N$ 10-Nitrodiacetyldeoxyalizarin (GOODALL and PERKIN), 476.

$C_{18}H_{14}O_5N_2$ *m*-Acetylbenzeneazo-β-naphthol-6-sulphonic acid, triammonium roseocobaltic salt (MORGAN, SMITH, and STANLEY), 1739.

$C_{18}H_{14}N_2S_2$ Substance, from sulphur and aniline (HODGSON), 1858.

$C_{18}H_{14}N_2S_3$ Substance, from sulphur and aniline (HODGSON), 1857.

$C_{18}H_{16}ON_2$ 5-Cyano-2-keto-1:5-diphenyl-4-methylpyrrolidine (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.

$C_{18}H_{16}O_3N_2$ Nitro-9-phenyltetrahydrocarbazole (LINNELL and PERKIN), 2459.

$C_{18}H_{16}O_4N_6$ Benzil disemioxamazone (WILSON and PICKERING), 1153.

$C_{18}H_{17}O_4N_3$ *p*-Nitrobenzeneazo-β-phenylpropionylacetone (MORGAN and PORTER), 1274.

$C_{18}H_{17}O_4Cl$ 3-Hydroxy-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium chloride ($+\frac{1}{2}H_2O$) (RIDGWAY and ROBINSON), 2242.

$C_{18}H_{17}O_5Cl$ 7-Hydroxy-3:5:4′-trimethoxy-2-phenylbenzopyrylium chloride (PRATT and ROBINSON), 196.

$C_{18}H_{17}O_6N$ 6-Nitro-3:4-dimethoxyphenyl 4-methoxystyryl ketone (LAWSON, PERKIN, and ROBINSON), 653.

$C_{18}H_{18}O_2N_2$ 2-Keto-1:5-diphenyl-4-methylpyrrolidine-5-carboxylamide (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.

$C_{18}H_{16}O_3N_2$ 11-Nitro-10-hydroxy-9-phenylhexahydrocarbazole (LINNELL and PERKIN), 2459.

$C_{18}H_{18}O_4N_2$ Phenacylsuccinic acid phenylhydrazone (ING and PERKIN), 1828.

$C_{18}H_{19}O_2N$ *o*-Anilinobenzoylvaleric acid (LINNELL and PERKIN), 2459.

$C_{18}H_{19}O_3N_3$ *iso*Nitrosomalon-*p*-toluidide methyl ethers (PLOWMAN and WHITELEY), 596.

$C_{18}H_{20}O_2N_2$ 4:4′-Dihydroxy-1:2:3:4:1′:2′:3′:4′-octahydro-4:4′-diquinolyl (CLEMO and PERKIN), 1620.

$C_{18}H_{21}O_4N_3$ *iso*Nitrosomalon-*p*-toluidide *O*-methyl ether hydrate (PLOWMAN and WHITELEY), 597.

$C_{18}H_{22}O_4N_4$ Phenylglucosazone, estimation of, volumetrically (KNECHT), 1545.

$C_{18}H_{21}O_2Cl$ *l*-Menthyl phenylchloroacetates, diastereoisomeric, racemisation of (MCKENZIE and SMITH), 1592.

$C_{18}H_{21}O_2Br$ *l*-Menthyl phenylbromoacetates, diastereoisomeric, racemisation of (MCKENZIE and SMITH), 1582.

$C_{18}H_{27}ON_3$ 6-Benzyl-*dl*-*iso*menthone semicarbazone (READ, SMITH, and HUGHESDON), 135.

$C_{18}H_{34}O_{12}Sn_2$ Pentapropionyl derivative of methylstannonic acid (LAMBOURNE), 2015.

## 18 IV

$C_{18}H_9O_{18}N_3Bi$ Hexanitrotriphenylbismuthine dinitrate (WILKINSON and CHALLENGER), 864.

$C_{18}H_{10}O_8N_6Br_2$ Dibromotetranitrodiphenyl-*p*-phenylenediamine (SANÉ and JOSHI), 2483.

$C_{18}H_{11}O_9N_4Bi$ Tetranitrotriphenylbismuthine dihydroxide (WILKINSON and CHALLENGER), 863.

$C_{18}H_{11}O_{14}N_6Bi$ Tetranitrotriphenylbismuthine dinitrate (WILKINSON and CHALLENGER), 862.

$C_{18}H_{12}OCl_2P$ Trichlorophenylphosphine oxides (CHALLENGER and WILKINSON), 2676.

$C_{18}H_{12}O_6N_3Bi$ Trinitrotriphenylbismuthine (WILKINSON and CHALLENGER), 863.

$C_{18}H_{13}O_{10}N_4Bi$ Dinitrotriphenylbismuthine dinitrate (WILKINSON and CHALLENGER), 863.

$C_{18}H_{15}Cl_3PBi$ Substance, from bismuth chloride and triphenylphosphine (CHALLENGER and PRITCHARD), 872.

$C_{18}H_{15}Cl_6PSb_2$ Substance, from antimony trichloride and triphenylphosphine (CHALLENGER and PRITCHARD), 871.

$C_{18}H_{16}OISb$ Triphenylstibine hydroxyiodide (WILKINSON and CHALLENGER), 860.

$C_{18}H_{17}O_2Cl_4Fe$ 8-Methoxy-2-phenyl-3:4′-dimethylbenzopyrylium ferrichloride (ROBINSON and DAS), 212.

$C_{18}H_{17}O_3Cl_4Fe$ 3:7-Dimethoxy-4-phenyl-2-methylbenzopyrylium ferrichloride (ALLAN and ROBINSON), 2194.

$C_{18}H_{17}O_4Cl_4Fe$ Trimethylapigenidin ferrichloride (PRATT, ROBINSON, and WILLIAMS), 205.

Trimethylgalangidin ferrichloride (PRATT and ROBINSON), 195.

$C_{18}H_{17}O_5Cl_4Fe$ 2′-Hydroxy-8:3′:4′-trimethoxy-2-phenylbenzopyrylium ferrichloride (ROBINSON and CRABTREE), 210.

$C_{18}H_{20}O_4N_2S_2$ 4:4′-Diacetylaminoditolyl 2:2′-disulphoxide (BERE and SMILES), 2362.

$C_{18}H_{22}O_4N_2S$ 3-Methylbenzo-(5:6)-9:10:11:12-tetrahydro-4-carboline methosulphate (G. M. and R. ROBINSON), 837.

### 18 V

$C_{18}H_9O_{12}N_6Cl_2Bi$ Hexanitrotriphenylbismuthine dichloride (WILKINSON and CHALLENGER), 864.

$C_{18}H_{11}O_8N_4Cl_2Bi$ Tetranitrotriphenylbismuthine dichloride (WILKINSON and CHALLENGER), 862.

$C_{18}H_{13}O_4N_2Cl_2Bi$ Dinitrotriphenylbismuthine dichloride (WILKINSON and CHALLENGER), 864.

## $C_{19}$ Group.

$C_{19}H_{12}N_2$ Acenaphthatolazine (SIRCAR and GUHA), 337.

$C_{19}H_{14}O_3$ 1-Toluoylnaphthalene-8-carboxylic acid (MASON), 2122.

$C_{19}H_{14}O_4$ Cinnamoyl derivative of 7-hydroxy-4-methylcoumarin (BARGER and EATON), 2410.

$C_{19}H_{15}N_3$ 1-Methyldihydroquinolenyl-2-quinolyl-2′-imine (HAMER), 1555.

$C_{19}H_{16}O_4$ 3-Acetyl-4-phenacyldihydrocoumarin (FORSTER and HEILBRON), 345.

4-*o*-Hydroxystyracyldihydrocoumarin (HEILBRON and FORSTER), 2066.

$C_{19}H_{16}N_2$ 16:17:18:19-Tetrahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1773.

$C_{19}H_{18}O_3$ 2:2′-Dimethoxydistyryl ketone (HEILBRON and FORSTER), 2067.

$C_{19}H_{18}O_5$ *ββ*-Dimethylglutarylfluorescein (DUTT and THORPE), 2531.

*as*-Methylethylsuccinylfluorescein (DUTT and THORPE), 2530.

$C_{19}H_{18}N_2$ 5:10:16:17:18:19-Hexahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1772.

$C_{19}H_{20}O_6$ 2-Hydroxy-4:6-dimethoxystyryl 3:4-dimethoxyphenyl ketone (PRATT, ROBINSON, and WILLIAMS), 206.

2-Hydroxy-3-methoxystyryl 2:3:4-trimethoxyphenyl ketone (ROBINSON and CRABTREE), 210.

$C_{19}H_{22}O_7$ Ethyl 5-phenyl-2:3-dihydrofuran-2:3:4-tricarboxylate (ING and PERKIN), 1826.

$C_{19}H_{24}O_7$ Ethyl *α*-benzoyltricarballylate (ING and PERKIN), 1828.

$C_{19}H_{26}N_2$ Quebrachamine, and its salts (FIELD), 1444.

### 19 III

$C_{19}H_8O_3Cl_6$ Hexachloroaurin (SPIERS), 455.

$C_{19}H_8O_3Br_6$ Hexabromoaurin (SPIERS), 455.

$C_{19}H_{10}O_4N_4$ 3:4-Dinitroacenaphthatolazine (SIRCAR and GUHA), 338.

$C_{19}H_{12}O_3Br_2$ Dibromoaurin (SPIERS), 457.

$C_{19}H_{15}O_5N$ 6:7-Dimethoxy-3′:4′-methylenedioxy-1-benzoyl*iso*quinoline, and its picrate (BUCK, HAWORTH, and PERKIN), 2182.

6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl*iso*quinoline (BUCK, HAWORTH, and PERKIN), 2181.

$C_{19}H_{16}ON_2$ Anhydro-2′-amino-9-phenyltetrahydrocarbazole-8-carboxylic acid (LINNELL and PERKIN), 2458.

5-Keto-5:10:16:17:18:19-hexahydroacrindoline, and its salts (CLEMO, PERKIN, and ROBINSON), 1771.

$C_{19}H_{16}O_3N_2$ 5-Cyano-2-keto-1:5-diphenyl-4-methylpyrrolidine-3-carboxylic acid (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.

$C_{19}H_{18}O_5N_2$ 6:7-Dimethoxy-3′:4′-methylenedioxy-1-benzoyl*iso*quinoline oxime (BUCK, HAWORTH, and PERKIN), 2183.

$C_{19}H_{16}O_5N_2$ 6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl*iso*quinoline oxime (BUCK, HAWORTH, and PERKIN), 2181.

$C_{19}H_{14}N_3Cl$ 2:2′-Diquinolylamine methochloride (HAMER), 1356.

$C_{19}H_{16}N_3I$ 2:2′-Diquinolylamine methiodide (HAMER), 1355.

$C_{19}H_{17}O_3P$ Triphenylmethylphosphinic acid, and its salts (BOYD and SMITH), 1477.

$C_{19}H_{17}O_5N$ 6:7-Dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline, and its salts (BUCK, HAWORTH, and PERKIN), 2182.

6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl-3:4-dihydro*iso*quinoline, and its hydriodide (BUCK, HAWORTH, and PERKIN), 2180.

$C_{19}H_{17}NBr_2$ β-Bromo-αβ-diphenylethylpyridinium bromide (BARNETT, COOK, and PECK), 1038.

$C_{19}H_{18}O_2N_2$ 2′-Amino-9-phenyltetrahydrocarbazole-8-carboxylic acid (LINNELL and PERKIN), 2458.

$C_{19}H_{18}O_5N_2$ 6:7-Dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline oxime (BUCK, HAWORTH and PERKIN), 2182.

6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl-3:4-dihydro*iso*quinoline oxime (BUCK, HAWORTH, and PERKIN), 2180.

$C_{19}H_{19}O_4N$ 1-Homopiperonyl-6:7-dimethoxy-3:4-dihydro*iso*quinoline, and its salts (BUCK and PERKIN), 1680.

1-Veratryl-6:7-methylenedioxydihydro*iso*quinoline, and its salts (HAWORTH, PERKIN, and RANKIN), 1694.

$C_{19}H_{19}O_4Cl$ 3:4′-Dimethoxy-8-ethoxy-2-phenylbenzopyrylium chloride ($+3\frac{1}{2}H_2O$) (RIDGWAY and RIDING), 2243.

$C_{19}H_{19}O_5Cl$ 3:5:7:4′-Tetramethoxy-2-phenylbenzopyrylium chloride (PRATT and ROBINSON), 197.

$C_{19}H_{20}ON_2$ 4-Acetonyl-2-methyl-γ-pyran phenylhydrazone (FORSTER and HEILBRON), 343.

$C_{19}H_{20}O_3N_2$ Diacetyl derivative of 9-β-hydroxyethylaminodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1793.

$C_{19}H_{20}O_5N_2$ Ethyl 6-carboxy-2′-acetylaminodiphenylamine-*N*-acetate (LINNELL and PERKIN), 2457.

$C_{19}H_{21}O_4N$ 1-Homopiperonyl-6:7-dimethoxytetrahydro*iso*quinoline, and its salts (BUCK and PERKIN), 1681.

1-Veratryl-6:7-methylenedioxytetrahydro*iso*quinoline, and its salts (HAWORTH, PERKIN, and RANKIN), 1695.

$C_{19}H_{21}O_5N$ Homopiperonylhomoveratrylamine (BUCK and PERKIN), 1680; (HAWORTH, PERKIN, and RANKIN), 1694.

$C_{19}H_{22}O_2N_2$ Diacetyldiphenylpropylenediamines (KIPPING and POPE), 2397.

$C_{19}H_{22}O_5N_2$ Diacetylhydratoacetylharmaline (NISHIKAWA, PERKIN, and ROBINSON), 663.

## 19 IV

$C_{19}H_{14}O_3NAs$ *N*-Benzoylphenarsazinic acid (BURTON and GIBSON), 2278.

$C_{19}H_{15}OCl_2P$ Triphenylmethoxyphosphorus dichloride, action of alcoholic potash on (BOYD and SMITH), 1477.

$C_{19}H_{18}ONBr$ β-Hydroxy-αβ-diphenylethylpyridinium bromide (BARNETT, COOK, and PECK), 1038.

$C_{19}H_{19}O_4Cl_4Fe$ 3:4′-Dimethoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and RIDING), 2244.

3:7-Dimethoxy-4-*p*-methoxyphenyl-2-methylbenzopyrylium ferrichloride (ALLAN and ROBINSON), 2194.

$C_{19}H_{19}O_5Cl_4Fe$ Tetramethyl-luteolidin ferrichloride (PRATT, ROBINSON, and WILLIAMS), 206.

3:5:7:4′-Tetramethoxy-2-phenylbenzopyrylium ferrichloride (PRATT and ROBINSON), 198.

$C_{19}H_{10}O_6Cl_4Fe$ 8:2′:3′:4′-Tetramethoxy-2-phenylbenzopyrylium ferrichloride (Robinson and Crabtree), 210.

19 V

$C_{19}H_{13}ONClAs$ 10-Chloro-5-benzoyl-5:10-dihydrophenarsazine (Shoesmith and Slater), 2279.

## $C_{20}$ Group.

$C_{20}H_{12}O_7$ Gallein, estimation of, volumetrically (Knecht), 1543.

$C_{20}H_{14}O_4$ Phenolphthalein, potassium salts (Bassett and Bagnall), 1366; estimation of, volumetrically (Knecht), 1543.

*o*-Vanillylidene-β-naphthacoumaranone (Ridgway and Robinson), 221.

$C_{20}H_{16}O_3$ 1:8-Xyloylnaphthalenecarboxylic acids (Mason), 2122.

$C_{20}H_{16}S_2$ 9-Anthryl-4-tolyl disulphide (Smiles and Gibson), 182.

$C_{20}H_{18}O_3$ 3-*o*-Hydroxyphenyl-5-*o*-hydroxystyryl-$\Delta^5$-*cyclo*hexen-1-one (Heilbron and Forster), 2066.

$C_{20}H_{18}O_4$ 4-*o*-Hydroxystyracyldihydrocoumarin methyl ether (Heilbron and Forster), 2067.

$C_{20}H_{24}O_7$ Ethyl 2-benzoyl*cyclo*pentane-1:2:3-tricarboxylate (Bernton, Ing, and Perkin), 1498.

$C_{20}H_{20}O_5$ *as*-Diethylsuccinylfluorescein (Dutt and Thorpe), 2530.

ββ-Methylethylglutarylfluorescein (Dutt and Thorpe), 2531.

20 III

$C_{20}H_{15}ON_3$ Acetyl-2:2′-diquinolylamine (Hamer), 1355.

$C_{20}H_{15}O_4N_3$ Carbanilino-*anti*-*p*-nitrobenzophenoneoxime (Brady and Mehta), 2304.

$C_{20}H_{16}O_4N_2$ 6-Carboxydiphenylamine-2′-*o*-aminobenzoic acid (Clemo, Perkin, and Robinson), 1780.

$C_{20}H_{16}O_4N_6$ 1:1′-(4:4′-Diphenylyl)-bis-5-methyl-1:2:3-triazole-4-carboxylic acid (Chattaway, Garton, and Parkes), 1990.

$C_{20}H_{17}ON$ 2:3:3-Triphenyldimethylene-1:2-oxaimine (Ingold and Weaver), 1461.

$C_{20}H_{17}O_4N$ ψ-Berberine, and its salts (Haworth, Perkin, and Rankin), 1686.

ψ-*epi*Berberine, and its salts (Buck and Perkin), 1675.

$C_{20}H_{17}O_5N$ Oxy-ψ-berberine (Haworth, Perkin, and Rankin), 1699.

Oxy-ψ-*epi*berberine (Buck and Perkin), 1685.

$C_{20}H_{18}ON_4$ Benzophenone-3-anilinosemicarbazone (Sutherland and Wilson), 2147.

$C_{20}H_{18}O_5Zr$ Zirconium bisbenzoylacetone (Morgan and Bowen), 1260.

$C_{20}H_{18}O_6N_2$ Dihydroxydiveratrocopyrine (Lawson, Perkin, and Robinson), 651.

$C_{20}H_{18}N_3I$ 1:1′-Dimethyl-2:2′-azocyanine iodide (Hamer), 1355.

$C_{20}H_{19}O_4N$ Dihydro-ψ-berberine, and its hydrochloride (Haworth, Perkin, and Rankin), 1698.

Dihydro-ψ-*epi*berberine, and its salts (Buck and Perkin), 1685.

$C_{20}H_{19}O_5N_3$ Aminohydroxydiveratrocopyrine (Lawson, Perkin, and Robinson), 652.

$C_{20}H_{20}O_4N_2$ Methyldiveratroharmyrine (Lawson, Perkin, and Robinson), 644.

$C_{20}H_{21}O_4N$ Papaveraldine, synthesis of (Buck, Haworth, and Perkin), 2176.

Tetrahydro-ψ-berberine, and its salts (Haworth, Perkin, and Rankin), 1696.

Tetrahydro-ψ-*epi*berberine, and its salts (Buck and Perkin), 1682.

$C_{20}H_{21}O_5N$ 3-Carbethoxyamino-8-methoxy-2-phenylbenzopyranyl methyl ether (Ridgway and Robinson), 2242.

6:7:3′:4′-Tetramethoxy-1-benzoyl-3:4-dihydro*iso*quinoline, and its salts (Buck, Haworth, and Perkin), 2184.

$C_{20}H_{22}O_5N_2$ 8-Methoxy-4-acetonyl-2-methyl-γ-pyran phenylhydrazone (FORSTER and HEILBRON), 346.

$C_{20}H_{22}O_6N_2$ Succinylrhodamine (DUTT and THORPE), 2532.

$C_{20}H_{22}O_6N_2$ 6:7:3′:4′-Tetramethoxy-1-benzoyl-3:4-dihydro*iso*quinoline oxime (BUCK, HAWORTH, and PERKIN), 2184.

$C_{20}H_{23}O_4N$ 6:7:3′:4′-Tetramethoxy-1-benzyl-3:4-dihydro*iso*quinoline, and its picrate (BUCK, HAWORTH, and PERKIN), 2183.

$C_{20}H_{27}O_{11}N$ Amygdalin, synthesis of (CAMPBELL and HAWORTH), 1337.

$C_{20}H_{29}N_2I$ Quebrachamine methiodide (FIELD), 1448.

$C_{20}H_{32}O_6N_4$ *l*-α-Phellandrene nitrosites (SMITH, CARTER, and READ), 933.

$C_{20}H_{44}O_{12}Sn_3$ Pentabutyryl derivatives of methylstannonic acid (LAMBOURNE), 2015.

## 20 IV

$C_{20}H_{13}O_3Cl_4Fe$ 8-Methoxy-β-naphthacoumarone-(β:α-2:3)-benzopyrylium ferrichloride (RIDGWAY and ROBINSON), 221.

$C_{20}H_{14}O_2N_4Cl_2$ *m*- and *p*-Chloropyrazole-blue (CHATTAWAY and STROUTS), 2425.

$C_{20}H_{15}O_3Cl_4Fe$ 8-Methoxy-2-α-naphthylbenzopyrylium ferrichloride (ROBINSON and DAS), 212.

$C_{20}H_{15}O_6N_2S_2$ 4-Nitro-2-sulphophenyldehydrothio-*p*-toluidinesulphonic acid, and its salts (PEACOCK), 1547.

$C_{20}H_{16}O_2N_4Cl_2$ Bis-1-*p*-chlorophenyl-3-methyl-5-pyrazolone (CHATTAWAY and STROUTS), 2426.

$C_{20}H_{16}O_7N_2As$ Nitrobenzoylaminobenzoyl-*p*-aminophenylarsinic acids, and their salts (KING and MURCH), 2606.

$C_{20}H_{17}O_6N_2S_2$ 4-Amino-2-sulphophenyldehydrothio-*p*-toluidinesulphonic acid, and its potassium salt (PEACOCK), 1547.

$C_{20}H_{18}O_2N_2S$ Toluene-*p*-sulphonylamino-5:10-dihydroacridine (CLEMO, PERKIN, and ROBINSON), 1791.

$C_{20}H_{18}O_4Br_2Sn$ Stannic bisbenzoylacetone dibromide (MORGAN and DREW), 379.

$C_{20}H_{18}O_6N_2As$ Aminobenzoylaminobenzoyl-*p*-aminophenylarsinic acids (KING and MURCH), 2607.

$C_{20}H_{19}N_2SI$ 2-Methyl-1′-ethylthiothiocyanine iodides (MILLS and ODAMS), 1919.

$C_{20}H_{27}O_3NS_2$ *d*- and *l*-Camphorylidenemethylsulphine-*p*-toluenesulphonylimine (MANN and POPE), 917.

# $C_{21}$ Group.

$C_{21}H_{14}O_4$ β-Naphthoyl derivative of 7-hydroxy-4-methylcoumarin (BARGER and EATON), 2410.

$C_{21}H_{17}N$ 2:6-Distyrylpyridine (SHAW), 2363.

$C_{21}H_{18}N_2$ 10:21-Etheno-5:10:16:17:18:19-hexahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1799.

$C_{21}H_{18}N_4$ Substance, from *p*-toluidine and 5-chloro-1:4-diphenyl-1:2:3-triazole, and also from aniline and 5-chloro-4-phenyl-1-*p*-tolyl-1:2:3-triazole (CARNELLEY and DUTT), 2478.

$C_{21}H_{20}O_3$ 3-*o*-Hydroxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one (HEILBRON and FORSTER), 2067.

$C_{21}H_{21}N_3$ Tetrahydrocarbazole-9:8-anhydropropionic acid phenylhydrazone (CLEMO and PERKIN), 1619.

$C_{21}H_{22}O_5$ ββ-Diethylglutarylfluorescein (DUTT and THORPE), 2531.

$C_{21}H_{22}N_2$ 10:21-Ethano-5:10:15:16:17:18:19:20-octahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1801.

21-Ethyl-15:16:17:18:19:20-hexahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1802.

$C_{21}H_{24}N_2$ Ethyloctahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1801.

$C_{21}H_{27}N$ 2:6-Di-β-phenylethylpiperidine, and its salts (SHAW), 2365.
$C_{21}H_{28}N_2$ Ethyldodecahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1803.

21 III

$C_{21}H_{12}O_5N_2$ Phenanthraquinone-4-azosalicylic acid (SIRCAR and ROY), 546.
$C_{21}H_{15}O_3N_3$ 2-Methylpyridine-3:4-dicarboxylanilide phenylimide (LAWSON, PERKIN, and ROBINSON), 639
$C_{21}H_{17}O_2Cl$ 3-Methoxy-2-α-naphthyl-6-methylbenzopyrylium chloride ($+3H_2O$) (RIDGWAY and ROBINSON), 219.
$C_{21}H_{17}NCl_2$ 2:6-Distyrylpyridine dichloride (SHAW), 2364.
$C_{21}H_{17}NBr_2$ 2:6-Distyrylpyridine dibromide (SHAW), 2364.
$C_{21}H_{19}ON_3$ Anhydro-5:10:16:17:18:19-hexahydroacrindoline-21-acetic acid (CLEMO, PERKIN, and ROBINSON), 1796.
$C_{21}H_{18}O_3N_2$ Anhydrocarboxyphenylaminotetrahydrocarbazoleacetic acid (CLEMO, PERKIN, and ROBINSON), 1784.
$C_{21}H_{20}O_2N_2$ Hexahydroacrindolineacetic acid (CLEMO, PERKIN, and ROBINSON), 1796.
$C_{21}H_{20}O_3N_2$ Ethyl 5-cyano-2-keto-1:5-diphenyl-4-methylpyrrolidine-3-carboxylate (HIGGINBOTHAM, LAPWORTH, and SIMPSON), 2342.
$C_{21}H_{20}O_4N_2$ 8-o-Carboxyphenylamino-1:2:3:4-tetrahydrocarbazole-9-acetic acid (CLEMO, PERKIN, and ROBINSON), 1783.
$C_{21}H_{20}O_5N_2$ Hydroxymethyldiveratrocopyrine (LAWSON, PERKIN, and ROBINSON), 650.
$C_{21}H_{21}Br_2Bi$ Tri-m-tolylbismuthine dibromide (CHALLENGER and PRITCHARD), 869.
$C_{21}H_{22}O_2N_2$ Strychnine (CLEMO, PERKIN, and ROBINSON), 1751.
$C_{21}H_{23}O_5N$ 3-Carbethoxyamino-8-methoxy-2-phenylbenzopyranyl ethyl ether (RIDGWAY and ROBINSON), 2242.
$C_{21}H_{24}ON_2$ 21-β-Hydroxyethyl-5:10:15:16:17:18:19:20-octahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1798.
$C_{21}H_{24}O_3N_2$ Glutarylrhodamine (DUTT and THORPE), 2533.
$C_{21}H_{24}O_7N_2$ Diacetylaminoveratrone (LAWSON, PERKIN, and ROBINSON), 641.
$C_{23}H_{26}O_4N_2$ Brucine (CLEMO, PERKIN, and ROBINSON), 1751.

21 IV

$C_{21}H_{16}ON_2S$ 2-Benzoyl-3-oxy(1)thionaphthen phenylhydrazone (HART and SMILES), 881.
$C_{21}H_{17}O_2Cl_4Fe$ 3-Methoxy-2-α-naphthyl-6-methylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 219.
$C_{21}H_{18}ON_3I$ Acetyl-2:2′-diquinolylamine monomethiodide (HAMER), 1355.
$C_{21}H_{22}OClSb$ Tri-m-tolylstibine hydroxychloride (CHALLENGER and PRITCHARD), 869.
$C_{21}H_{22}O_2N_2S$ *dl*-Benzenesulphonyldiphenylpropylenediamines, and their hydrochlorides (KIPPING and POPE), 2398.
$C_{21}H_{22}NCl_4I$ Tribenzylammonium tetrachloroiodide (CHATTAWAY and GARTON), 188.
$C_{21}H_{32}O_4N_2S$ Quebrachamine methosulphate (FIELD), 1448.

## $C_{22}$ Group.

$C_{22}H_{12}N_2$ Acenaphthanaphthazine (SIRCAR and GUHA), 337.
$C_{22}H_{16}N_4$ 3:6-Diamino-7:12-dihydronaphthanaphthazine (SIRCAR and GUHA), 340.
$C_{22}H_{20}O$ 2:5-Diphenylacetylenyl-2:5-dimethyltetrahydrofuran (WILSON and HYSLOP), 1557.
$C_{22}H_{20}O_3$ Trimethylaurin (SPIERS), 459.

$C_{22}H_{21}O_5$ *as-cyclo*Hexanesuccinylfluorescein (DUTT and THORPE), 2530.

$C_{22}H_{32}O_3$ 3-*o*-Methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one (HEILBRON and FORSTER), 2067.

$C_{22}H_{32}O_4$ Ethyl 5-phenyl-3-*o*-methoxyphenyl-$\Delta^5$-*cyclo*hexen-1-one-2-carboxylate (FORSTER and HEILBRON), 346.

$C_{22}H_{32}O_{13}$ Ethyl *dl*-amygdalinate (CAMPBELL and HAWORTH), 1340.

## 22 III

$C_{22}H_{10}O_4N_4$ 3:4-Dinitroacenaphthanaphthazine (SIRCAR and GUHA), 338.

$C_{22}H_{14}O_3S$ 2-Benzoyl-3-benzoyloxy(1)thionaphthen (HART and SMILES), 881.

$C_{22}H_{17}O_3N$ Diphenylsuccinanils (WREN and BURROWS), 1935.

$C_{22}H_{17}O_3Br_3$ Tribromotrimethylaurin (SPIERS), 459.

$C_{22}H_{19}O_3Cl$ 3-Methoxy-8-ethoxy-2-*α*-naphthylbenzopyrylium chloride ($+ 2H_2O$) (RIDGWAY and ROBINSON), 220.

$C_{22}H_{19}ON_3$ Phenyl *β*-phenylstyryl ketone semicarbazones (WILSON and MACAULAY), 843.

$C_{22}H_{19}O_3N$ *r*-Diphenylsuccinalic acid, resolution of (WREN and BURROWS), 1934.

$C_{22}H_{20}ON_2$ Anilo-2-carboxy-4:6-dimethylbenzaldehyde anilide (PERKIN and TAPLEY), 2436.

$C_{22}H_{20}O_2N_2$ *s*-Diacetyldiphenyl-*o*-phenylenediamine (CLEMO, PERKIN, and ROBINSON), 1781.

Diacetyltetrahydro-4:4′-diquinolyl (CLEMO and PERKIN), 1622.

$C_{22}H_{20}O_4Se_2$ Selenium *ω*-phenylacetylacetone (MORGAN and PORTER), 1272.

$C_{22}H_{22}O_4N_2$ Dimethyldiveratrocopyrine, and its salts (LAWSON, PERKIN, and ROBINSON), 646.

$C_{22}H_{25}O_3N$ *ON*-Dibenzoyl-*α*- and -*β*-vinyldiacetonalkamines (KING), 57.

$C_{22}H_{25}O_6N$ 3-Carbethoxyamino-4′-methoxy-8-ethoxy-2-phenylbenzopyranyl methyl ether (RIDGWAY and ROBINSON), 2242.

$C_{22}H_{26}O_3N_2$ *as*-Dimethylsuccinylrhodamine (DUTT and THORPE), 2532.

## 22 IV

$C_{22}H_{10}O_7N_4S$ 3:4-Dinitroacenaphthanaphthazine-5′-sulphonic acid (SIRCAR and GUHA), 339.

$C_{22}H_{12}O_3N_2S$ Acenaphthanaphthazine-5′-sulphonic acid (SIRCAR and GUHA), 338.

$C_{22}H_{19}O_3Cl_4Fe$ 3-Methoxy-8-ethoxy-2-*α*-naphthylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 220.

$C_{22}H_{20}O_4Cl_2Cu$ Copper 3-chloro-*ω*-phenylacetylacetone (MORGAN and PORTER), 1272.

$C_{22}H_{21}O_5N_3S$ Acetyl-2:2′-diquinolylamine dimethosulphate (HAMER), 1355.

$C_{22}H_{22}O_3N_2S$ *β*-Hydroxyethyl derivative of toluene-*p*-sulphonylaminodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1791.

$C_{22}H_{26}O_8N_2S$ Methyldiveratroharmyrine methosulphate (LAWSON, PERKIN, and ROBINSON), 644.

## 22 V

$C_{22}H_{21}O_2N_2ClS$ *β*-Chloroethyl derivative of toluene-*p*-sulphonylaminodihydroacridine (CLEMO, PERKIN, and ROBINSON), 1791.

# $C_{23}$ Group.

$C_{23}H_{18}O_2$ 4-Phenacyl-2-phenyl-*γ*-pyran (FORSTER and HEILBRON), 344.

$C_{23}H_{23}O_5$ *β-cyclo*Hexaneglutarylfluorescein (DUTT and THORPE), 2531.

## 23 III

$C_{23}H_{12}O_5Br_6$ Hexabromodiacetylaurin (SPIERS), 456.

$C_{23}H_{19}O_2N$ Diphenylsuccino-*p*-tolils (WREN and BURROWS), 1936.

$C_{23}H_{19}O_4N$ *d*-β-Benzoyl-α-phenylethylphthalamic acid (McKenzie and Tudhope), 929.

$C_{23}H_{20}ON_4$ Acetyl derivative from substance $C_{21}H_{18}N_4$ (Carnelley and Dutt), 2481.

$C_{23}H_{21}O_3N$ *r*-Diphenylsuccino-*p*-toluidic acid, resolution of (Wren and Burrows), 1936.

$C_{23}H_{22}O_2N_2$ Ethyl tetrahydroacrindoline-21-acetate (Clemo, Perkin, and Robinson), 1800.

$C_{23}H_{22}O_3N_2$ Anhydro-8-*o*-carbethoxyphenylamino-1:2:3:4-tetrahydrocarbazole-9-acetic acid (Clemo, Perkin, and Robinson), 1783.

Ethyl anhydrocarboxyphenylaminotetrahydrocarbazoleacetate (Clemo, Perkin, and Robinson), 1784.

$C_{23}H_{22}O_5N_2$ Acetyl derivative of 8-*o*-carboxyphenylamino-1:2:3:4-tetrahydrocarbazole-9-acetic acid (Clemo, Perkin, and Robinson), 1783.

$C_{23}H_{25}ON_3$ Acetylethyloctahydroacrindoline (Clemo, Perkin, and Robinson), 1802.

$C_{23}H_{28}O_3N_2$ ββ-Dimethylglutarylrhodamine (Dutt and Thorpe), 2533.

*as*-Methylethylsuccinylrhodamine (Dutt and Thorpe), 2532.

$C_{23}H_{30}ON_2$ Acetylethyldodecahydroacrindoline (Clemo, Perkin, and Robinson), 1803.

## $C_{24}$ Group.

$C_{24}H_{16}O$ Diphenylacetonaphthone (McKenzie and Dennler), 2109.

α-Naphthyldeoxybenzoin (McKenzie and Dennler), 2108.

Substance, from dehydration of αβ-dihydroxy-αβ-diphenyl-β-naphthylethane (McKenzie and Roger), 853.

$C_{24}H_{16}O_3$ 4-Phenacyl-2-phenyl-γ-pyran-3-carboxylic acid (Forster and Heilbron), 344.

$C_{24}H_{22}O_6$ Phthaleins, from hemipinic anhydride and *o*- and *m*-cresols (Simonsen), 723.

$C_{24}H_{24}O_4$ Diethoxytrimethylenedibenzo*spiro*pyran (Ridgway and Robinson), 218.

$C_{24}H_{24}O_5$ Ethyl 3-*o*-methoxyphenyl-5-*o*-hydroxystyryl-$\Delta^5$-*cyclo*hexen-1-one-2-carboxylate (Heilbron and Forster), 2067.

$C_{24}H_{28}O$ 2-Benzylidene-6-benzyl-*dl-iso*menthone (Read, Smith, and Hughesdon), 136.

$C_{24}H_{32}O$ 2:6-Dibenzyl-*dl-iso*menthol (Read, Smith, and Hughesdon), 136.

### 24 III

$C_{24}H_{10}O_4N_6$ 3:4-Dinitroacenaphthaphenaziazine (Sircar and Guha), 338.

$C_{24}H_{21}ON$ β-Hydroxy-αβ-diphenyl-β-naphthylethylamine, deamination of (McKenzie and Dennler), 2105.

$C_{24}H_{24}O_4Se_2$ Selenium β-phenylpropionylacetone (Morgan and Porter), 1275.

$C_{24}H_{26}O_4Cu$ Copper β-phenylpropionylacetone (Morgan and Porter), 1274.

$C_{24}H_{30}O_3N_2$ *as*-Diethylsuccinylrhodamine (Dutt and Thorpe), 2532.

ββ-Methylethylglutarylrhodamine (Dutt and Thorpe), 2533.

$C_{24}H_{31}O_3N$ Benzyl-*dl-iso*menthol phenylurethanes (Read, Smith, and Hughesdon), 133.

$C_{24}H_{48}O_{12}Sn_6$ Hexapropionyl derivative of methylstannonic acid (Lambourne), 2015.

### 24 IV

$C_{24}H_{17}O_3Cl_4Fe$ 3-Methoxy-2-α-naphthylnaphtha-(2:1)-pyrylium chloride (Ridgway and Robinson), 220.

$C_{24}H_{24}O_4Cl_2Cu$ Copper chloro-β-phenylpropionylacetone (Morgan and Porter), 1274.

$C_{24}H_{25}O_4Cl_4Fe$ 5-Ethoxy-4-(2-hydroxy-3-ethoxybenzylidene)-1:2:3-tetrahydroxanthylium ferrichloride (+ $H_2O$) (RIDGWAY and ROBINSON), 218.

$C_{24}H_{26}O_4N_2S$ Dimethylacetalylsulphonylamino-5:10-dihydroacridine (CLEMO, PERKIN, and ROBINSON), 1794.

### 24 V

$C_{24}H_{20}O_3NCl_4Fe$ 3-Benzoylamino-8-ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 216.

## $C_{25}$ Group.

$C_{25}H_{26}O_5$ Ethyl 3-*o*-methoxyphenyl-5-*o*-methoxystyryl-$\Delta^5$-*cyclo*hexen-1-one-2-carboxylate (HEILBRON and FORSTER), 2067.

$C_{25}H_{44}O_6$ Anhydro-methylglucoside mono-oleate (IRVINE and GILCHRIST), 7.

$C_{25}H_{52}O_3$ Tri-*l*-$\beta$-octyl orthoformate, rotatory power of (HUNTER), 1394.

### 25 III

$C_{25}H_{14}O_5N_2$ 2- and 4-Hydroxyphenanthraquinoneazo-3-naphthoic acids (SIRCAR and ROY), 545.

$C_{25}H_{16}O_7Br_6$ Hexabromotriacetylaurin (SPIERS), 456.

$C_{25}H_{18}NCl$ Substance, from carbazole, benzophenone, and phosphoryl chloride (DUTT), 807.

$C_{25}H_{22}O_4N_2$ Phenyldiveratroharmyrine (LAWSON, PERKIN, and ROBINSON), 642.

$C_{25}H_{23}O_5N$ Dipiperonylidene-$\psi$-pelletierine (MENZIES and ROBINSON), 2168.

$C_{25}H_{25}N_2I$ 1:1′-Diethyl-2:4′-carbocyanine iodide (MILLS and ODAMS), 1919.

$C_{25}H_{26}O_6N_2$ *N*-Phenacyldiaminoveratrone (LAWSON, PERKIN, and ROBINSON), 641.

$C_{25}H_{28}O_3N_2$ Diacetyl derivative of $\beta$-hydroxyethyloctahydroacrindoline (CLEMO, PERKIN, and ROBINSON), 1799.

$C_{25}H_{33}O_3N$ $\beta\beta$-Diethylglutarylrhodamine (DUTT and THORPE), 2533.

### 25 V

$C_{25}H_{22}O_4NCl_4Fe$ 3-Benzoylamino-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride (RIDGWAY and ROBINSON), 217.

## $C_{26}$ Group.

$C_{26}H_{20}O_3$ Ditoluoylnaphthalene or Ditolylnaphthalide (MASON), 2122.

$C_{26}H_{46}O_6$ Di-*l*-menthyl-*l*-dimethoxysuccinate (WREN and HUGHES), 1742.

Methyl anhydro-methylglucoside mono-oleate (IRVINE and GILCHRIST), 8.

### 26 III

$C_{26}H_{20}O_4N_2$ *o*-Phenylenediveratrocopyrine, and its acetate (LAWSON, PERKIN, and ROBINSON), 649.

$C_{26}H_{23}O_5N_3$ Nitrobenzoyl derivative of 6:7-dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline (BUCK, HAWORTH, and PERKIN), 2182.

$C_{26}H_{23}O_7N$ Benzoyl derivative of 6:7-dimethoxy-3′:4′-methylenedioxy-1-benzoyl-3:4-dihydro*iso*quinoline (BUCK, HAWORTH, and PERKIN), 2182.

Benzoyl derivative of 6:7-methylenedioxy-3′:4′-dimethoxy-1-benzoyl-3:4-dihydro-*iso*quinoline (BUCK, HAWORTH, and PERKIN), 2181.

$C_{26}H_{31}O_3N_2$ *as-cyclo*Hexanesuccinylrhodamine (DUTT and THORPE), 2532.

### 26 IV

$C_{26}H_{32}O_{10}N_{16}Co$ Metachrome brown B cobaltic lake (MORGAN and SMITH), 1737.

## $C_{27}$ Group.

$C_{27}H_{24}O_4N_2$ Phenylmethyldiveratrocopyrine (LAWSON, PERKIN, and ROBINSON), 648.

$C_{27}H_{37}O_7N$ Benzoyl derivative of 6:7:3′:4′-tetramethoxy-1-benzoyl-3:4-dihydro*iso*-quinoline (BUCK, HAWORTH, and PERKIN), 2184.

$C_{27}H_{29}N_2I$ 2′:4-Dimethyl-1:1′-diethyl-2:4′-carbocyanine iodide (MILLS and ODAMS), 1920.

$C_{27}H_{33}O_3N_2$ *β-cyclo*Hexaneglutarylrhodamine (DUTT and THORPE), 2533.

27 IV

$C_{27}H_{17}O_2N_2Cl$ Flavinduline-*o*-carboxylic acid (CLEMO, PERKIN, and ROBINSON), 1780.

## $C_{28}$ Group.

$C_{28}H_{18}O_6$ 3:4:5′:6′-Tetrahydroxydianthrone (GOODALL and PERKIN), 474.

28 III

$C_{28}H_{16}O_8N_4$ Phenanthraquinonebisazosalicylic acids (SIRCAR and ROY), 546.

$C_{28}H_{17}N_2Cl$ Naphthylacenaphthaphenazonium chloride (SIRCAR and GUHA), 339.

Phenylacenaphthanaphthazonium chloride (SIRCAR and GUHA), 339.

$C_{28}H_{18}O_8S_2$ Dianthronedisulphonic acids, and their salts (BARNETT and MATTHEWS), 1080.

$C_{28}H_{18}O_{14}S_4$ Dianthronetetrasulphonic acids, and their salts (BARNETT and MATTHEWS), 1081.

$C_{28}H_{23}O_{13}N_3$ 6-Nitropiperonal-6-nitropiperonoylhydrocotarnine (G. M. and R. ROBINSON), 840.

28 IV

$C_{28}H_{15}O_4N_4Cl$ Phenyl-3:4-dinitroacenaphthanaphthazonium chloride (SIRCAR and GUHA), 339.

## $C_{29}$ Group.

$C_{29}H_{26}O_2N_2$ Dibenzoyldiphenylpropylenediamines (KIPPING and POPE), 2398.

## $C_{30}$ Group.

$C_{30}H_{18}O_6$ 2:7′-Dimethoxy-1:1′-dianthraquinonyl (HALLER and PERKIN), 237.

$C_{30}H_{21}Sb$ Tri-α-naphthylstibine (CHALLENGER and PRITCHARD), 869.

$C_{30}H_{28}O_2$ *l*-Di-diphenylmethylethylene oxide (MCKENZIE and ROGER), 2153.

$C_{30}H_{28}N_4$ Dibenzylketazine (WILSON and PICKERING), 1154.

30 III

$C_{30}H_{21}Cl_2Sb$ Tri-α-naphthylstibine dichloride (CHALLENGER and PRITCHARD), 869.

$C_{30}H_{21}Br_2Sb$ Tri-α-naphthylstibine dibromide (CHALLENGER and PRITCHARD), 869.

$C_{30}H_{60}O_{18}Sn_6$ Hexabutyryl derivatives of methylstannonic acid (LAMBOURNE), 2015.

30 IV

$C_{30}H_{22}O_4Br_2Sn$ Stannic bisdibenzoylmethane dibromide (MORGAN and DREW), 379.

$C_{30}H_{27}O_6ClZr$ Zirconium tribenzoylacetone chloride (MORGAN and BOWEN), 1258.

30 V

$C_{30}H_{23}O_3N_4ClP$ Substance, from phosphorus pentachloride and anhydro-5:10-dihydroacridine-9-aminoacetic acid (CLEMO, PERKIN, and ROBINSON), 1789.

## $C_{31}$ Group.

$C_{31}H_{22}N_2$ Substance, from carbazole and benzaldehyde (DUTT), 803.
$C_{31}H_{21}N_2Cl$ Substance, from carbazole, benzaldehyde, and hydrochloric acid (DUTT), 803.
$C_{31}H_{22}ON_2$ Substance, from carbazole, benzaldehyde, and pyridine (DUTT), 803.

## $C_{32}$ Group.

$C_{32}H_{16}O_6$ 3:6′-Dihydroxynaphthadianthrone (HALLER and PERKIN), 238.
$C_{32}H_{18}O_8$ 2:7′-Dihydroxy-1:1′-dianthraquinonyl (HALLER and PERKIN), 236.
$C_{32}H_{26}O_6$ 3:4:5′:6′-Tetramethoxydianthrone (GOODALL and PERKIN), 475.
$C_{32}H_{32}O_2$ *l*-Di-diphenylethylethylene oxide (MCKENZIE and ROGER), 2154.

### 32 III

$C_{32}H_{17}O_6I$ 5-Iodo-3:6′-dihydroxyhelianthrone (HALLER and PERKIN), 237.
$C_{32}H_{24}N_5Cl$ 2:7-Diamino-11-anilinoflavinduline chloride (SIRCAR and ROY), 544.
$C_{32}H_{26}O_4N_2$ Diphenyldiveratrocopyrine, and its salts (LAWSON, PERKIN, and ROBINSON), 648.

### 32 IV

$C_{32}H_{20}O_4N_5Cl$ 2:7-Dinitro-11-anilinoflavinduline chloride (SIRCAR and ROY), 544.
$C_{32}H_{20}N_3ClBr_2$ 4:5-Dibromo-11-anilinoflavinduline chloride (SIRCAR and ROY), 544.
$C_{32}H_{21}O_2N_4Cl$ 2-Nitro-11-anilinoflavinduline chloride (SIRCAR and ROY), 544.

## $C_{34}$ Group.

$C_{34}H_{22}O_2$ *αα*-Tetraphenylacetylenylethylene glycol (WILSON and HUGHES), 1557.

### 34 III

$C_{34}H_{38}O_5Be$ Beryllium benzoylcamphor, mutarotation of, and its compound with chloroform (BURGESS and LOWRY), 2081.

### 34 IV

$C_{34}H_{26}O_8Cl_5Fe$ 3-Hydroxy-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride ($+H_2O$) (RIDGWAY and RIDING), 2243.

## $C_{36}$ Group.

$C_{36}H_{26}O_2$ *ααδδ*-Tetraphenylacetylenyl-*αδ*-butylene glycol (WILSON and HYSLOP), 1557.
$C_{36}H_{60}O_{30}$ *β*-Hexa-amylose, molecular structure of (IRVINE, PRINGSHEIM, and MACDONALD), 943.

### 36 III

$C_{36}H_{20}O_8N_4$ Phenanthraquinonebis(1-azo-2- and -4-hydroxy-3-naphthoic acids) (SIRCAR and ROY), 546.

## $C_{40}$ Group.

$C_{40}H_{30}O_{12}$ Hexa-acetyldianthranol (GOODALL and PERKIN), 474.
$C_{40}H_{34}O_{10}$ Tetra-acetyldiethoxydianthranol (GOODALL and PERKIN), 474.

## $C_{41}$ Group.

$C_{41}H_{34}O_{11}N_6As_2$ *s*-Carbamides of aminobenzoylaminobenzoyl-*p*-aminophenylarsinic acids (KING and MURCH), 2610.

## $C_{42}$ Group.

$C_{42}H_{76}O_7$ Mannitan dioleate (IRVINE and GILCHRIST), 13.

### 42 III

$C_{42}H_{30}O_{16}Br_{12}$ Bromolignin (POWELL and WHITTAKER), 364.
$C_{42}H_{29}O_{22}N_3$ Nitrolignin (POWELL and WHITTAKER), 364.

## $C_{43}$ Group.

$C_{43}H_{78}O_7$ Methyl mannitan dioleate (IRVINE and GILCHRIST), 13.

### 43 III

$C_{43}H_{32}O_{16}Cl_{12}$ Chlorolignin (POWELL and WHITTAKER), 363.

## $C_{45}$ Group.

$C_{45}H_{33}O_6ClZr$ Zirconium trisdibenzoylmethane chloride, and its salts (MORGAN and BOWEN), 1256.

## $C_{48}$ Group.

$C_{48}H_{54}O_{16}$ Methyl-lignin (POWELL and WHITTAKER), 363.

### 48 V

$C_{48}H_{27}O_{21}N_6S_2Co$ Oxidised diamond black PV cobaltic lake ($+3H_2O$), and its salts (MORGAN and SMITH), 1738.
$C_{48}H_{33}O_{18}N_6S_3Cr$ Diamond black PV chromic lake ($+3H_2O$) (MORGAN and SMITH), 1737.

## $C_{51}$ Group.

$C_{51}H_{33}O_{18}N_6S_3Co$ *o*-Carboxybenzeneazo-β-naphthol-6-sulphonic acid cobaltic lake, cobaltic salt of (MORGAN, SMITH, and STANLEY), 1739.

## $C_{54}$ Group.

$C_{54}H_{51}O_{28}N_3$ Acetylnitrolignin (POWELL and WHITTAKER), 364.

## $C_{60}$ Group.

$C_{60}H_{39}O_{15}N_6S_3Co$ Palatine chrome black 6 B cobaltic lake ($+3H_2O$), and its cobaltic salt (MORGAN and SMITH), 1737.
$C_{60}H_{39}O_{15}N_6S_3Cr$ Palatine chrome black 6 B chromic lake ($+3H_2O$) (MORGAN and SMITH), 1736.
$C_{60}H_{45}O_{18}N_{12}S_3Co$ Eriochrome red B cobaltic lake ($+3H_2O$), and its salts (MORGAN and SMITH), 1736.
$C_{60}H_{45}O_{15}N_{12}S_3Cr$ Eriochrome red B chromic lake (MORGAN and SMITH), 1735.

## ERRATA.

### Vol. 123 (Trans., 1923).

| Page | | Line | |
|---|---|---|---|
| 1912 | | 16 | *for* " Vignerie " *read* " Viguerie." |
| ,, | (last col.) | 17—25 | *for* " 118·05, 90·92, non dosée, 27·02, (S. Humages) non dosée, non dosée, 65·96, non dosée, 60·74 " *read* " 132·5, 107·0, 55·5, 28·0, (S. Etuves) 8·6, non dosée, 76·7, 8·2, 82·5." |
| 1914 | (last col.) | 16 | *for* " 141·50 " *read* " 161·4." |
| 1917 | | 24* | *for* " 6·077 10·020 " *read* " 6,077 10,020." |
| ,, | | 12* | *for* " 65,486 " *read* " 69,800." |
| 1918 | | 4 | |
| 1923 | Table IV, last col. | | *for* " Ar " *read* " Kr." |
| ,, | | 20* | *for* " 1·8 " *read* " 1·2." |
| ,, | | 19* | *for* " No. 8 " *read* " No. 2." |
| ,, | | 1* | *for* " 24·814 " *read* " 24,814." |
| 1926 | | 18* | *for* " 1·000 " *read* " 1·004." |
| ,, | | 17* | *for* " 1 " *read* " 1·004." |
| 1930 | | 9* | *for* " Shutt " *read* " Strutt." |
| 1931 | | 18 | *for* " $1{\cdot}5^{-12}$ " *read* " $1{\cdot}5 \times 10^{-12}$." |
| ,, | | 19 | *for* " $1{\cdot}2^{-5}$ " *read* " $1{\cdot}2 \times 10^{-5}$." |
| 1932 | | 3* | *for* " Leche " *read* " Zeche." |
| 1936 | Table XI, 2nd col. | | *for* " 1·18 " *read* " 1·195." |
| ,, | ,, 3rd col. | | *for* " 0·82, 0·97, 0·85, 1·72, 1·38 " *read* " 0·81, 0·96, 0·84, 1·70, 1·36." |
| 1938 | | 15 | *for* " Ysère " *read* " Isère." |
| 1939 | | 19 | *for* " 0·25 " *read* " 0·26." |
| 1940 | | 4 | *for* " notablement plus élevó " *read* " du même ordre." |
| ,, | | 5 | *for* " Anzin, 4380 mètres cubes " *read* " Vaux-en-Bugey, 20,747 mètres cubes." |
| ,, | | 14 | *add* " Les recherches relatives à l'hélium des gaz naturels du Canada et des Etats-Unis ont fait l'objet d'importantes publications d'ensemble dues au Professeur MacLennan et associés (Department of Mines, Bull. 31, Ottawa, 1920) et à G. S. Rogers (Department of the Interior, Professional Paper No. 121, Washington, 1921)." |
| 1941 | | 5 | *for* " Ponzzoles " *read* " Pouzzoles." |
| ,, | | 11* | *for* " toute relation de l'azote " *read* " inertie toute relative de l'azote." |
| 2795 | | 21 | *for* " former " *read* " latter." |
| ,, | | 26 | *for* " latter " *read* " former." |
| 3155 | | 3 | *for* " 1·5/4·22 " *read* " 1·22/1·5." |
| 3256 | | 4 | *for* " George " *read* " Gray." |
| 3349 | | 2* | *for* " 248 " *read* " 428." |

* From bottom.

## VOL. 125 (1924).

| Page | Line | |
|---|---|---|
| 426 | 4 | *for* "$1{\cdot}3 \times 10^{-12}$" *read* "$1{\cdot}07 \times 10^{-12}$." |
| ,, | 5 | *for* "$1{\cdot}0 \times 10^{-12}$" *read* "$1{\cdot}03 \times 10^{-12}$." |
| 1049 | 13* | *for* "*m*-hydroxybenzoic" *read* "*m*-nitrobenzoic." |
| 1323 | 11 | *for* "4·9" *read* "4·0." |
| 1543 | 14 | *for* "tetralene" *read* "tetralin." |
| ,, | 15* | *for* "phenolphthalein" *read* "phenolphthalin." |
| 1756 | 3 | *for* "lower" *read* "upper." |
| 1756 | 4 | *for* "anhydrocarboxyphenylaminotetrahydrocarb- |
| 1784 | 1 | azoleacetic acid" *read* "5-keto-5:10:16:17:18:19-hexahydroacrindoline-21-acetic acid." |
| 1780 | 5* | *for* "*o*-Phenylenediamine (2·7 gms)" *read* "2'-Aminodiphenylamine-6-carboxylic acid (13 gms)." |
| 1928 | 22 | *for* "Toironen" *read* "Toivonen." |
| 1934 | 6 | (and throughout the paper) *for* "diphenylsuccinalic" *read* "diphenylsuccinanilic." |
| 1960 | 10 | *delete* "MINES DEPARTMENT EXPERIMENTAL |
| 1963 | 9 | STATION, SHEFFIELD." |
| 2377 | | Formula II, *for* "$CH_2Br$" *read* "$CH_3$." |
| ,, | 2 | *for* "Bromocampholenic" *read* "Campholenic." |

* From bottom.

*List of Symbols Recommended by the Working Committee of the International Commission for the Unification of Physico-chemical Symbols* (1914). [See Trans., 1921, **119**, 502—512.]

### 1. *Mathematical Symbols.*

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Base of natural (Napierian) logarithms ... | $e$ | |
| Diameter ..... | $d$ | |
| Radius ..... | $r$ | |
| Ratio of circumference to diameter ..... | $\pi$ | |
| Summation ..... | $\Sigma$ | |
| Variation ..... | $\delta$ | |
| Total differential ..... | $d$ | |
| Partial differential ..... | $\partial$ | |

### 2. *Universal Constants.*

| | | |
|---|---|---|
| Acceleration due to gravity ..... | $g$ | |
| Mechanical equivalent of heat ..... | $J$ | |
| Avogadro's constant [number of molecules in 1 gram-molecule (mole)] ..... | $N$ | |
| Gas constant per mole ..... | $R$ | |
| Faraday's constant (number of coulombs per gram-equivalent of an ion) ..... | $F$ | |
| Charge on an electron ..... | $e$ | |

### 3. *General Physics and Chemistry.*

| | | |
|---|---|---|
| Length ..... | $l$ | |
| Height ..... | $h$ | |
| Mass ..... | $m$ | |
| Time ..... | $t$ | |
| Volume ..... | $v$, $V$ | |
| Density (mass per unit volume) ..... | $d$ | $D$ |
| Pressure ..... | $p$, $P$ | |
| Concentration ..... | $c$, $C$ | |
| Mole fraction ..... | $x$ | |
| Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density ..... | $p_c$, $v_c$; $t_c$, $T_c$; $d_c$ | |
| Reduced quantities: pressure, volume, temperature, density ..... | $p_r$, $v_r$; $t_r$, $T_r$, $d$ | |
| van der Waals's constants ..... | $a$, $b$ | |
| Fluidity ..... | $\phi$ | |
| Viscosity ..... | $\eta$ | |
| Surface tension ..... | $\gamma$ | $\sigma$ |
| Diffusion coefficient ..... | $\Delta$ | |
| Atomic weight ..... | $A$ | |
| Molecular weight ..... | $M$ | |
| Velocity coefficient of reaction ..... | $k$ | |
| Equilibrium constant ..... | $K$, ($K_c$, $K_p$) | |
| van't Hoff coefficient ..... | $i$ | |
| Degree of dissociation (electrolytic, thermal, etc.) ..... | $\alpha$ | |

### 4. *Heat and Thermodynamics.*

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Temperature (centigrade) | $t$ | $\theta$ |
| Temperature (absolute) | $T$ | |
| Critical temperature | $t_c$, $T_c$ | |
| Reduced temperature | $t_r$, $T_r$ | |
| Critical solution temperature | $t_{cs}$, $T_{cs}$ | |
| Quantity of heat | $Q$ | |
| Entropy | $S$ | |
| Specific heat | $c$ | |
| Specific heat at constant pressure | $c_p$ | |
| Specific heat at constant volume | $c_v$ | |
| Ratio of specific heats, $c_p : c_v$ | $\gamma$ | |
| Molecular heat | $C$ | |
| Molecular heat at constant pressure | $C_p$ | |
| Molecular heat at constant volume | $C_v$ | |
| Latent heat per gram | $l$ | |
| Latent heat per mole | $L$ | |
| Maximum work (diminution of free energy) | $A$ | |

### 5. *Optics.*

| | | |
|---|---|---|
| Wave-length of light | $\lambda$ | |
| Refractive index | $n$ | $n_r$ |
| Specific refractive power (Gladstone and Dale) | $r_G$, $[r_G]^t_\lambda$ | |
| Specific refractive power (Lorentz and Lorenz) | $r_L$, $[r_L]^t_\lambda$ | |
| Molecular refractive power | $R_G$, $R_L$<br>$[R_G]^t_\lambda$, $[R_L]^t_\lambda$ | |
| Angle of optical rotation | $\alpha$ | |
| Specific rotatory power | $[\alpha]$ | |
| Molecular rotatory power | $M[\alpha]$ | |
| Specific magnetic rotation | $[\omega]$ | |
| Molecular magnetic rotation | $M[\omega]$ | |

### 6. *Electricity and Magnetism.*

| | | |
|---|---|---|
| Quantity of electricity | $Q$ | |
| Current intensity | $I$ | |
| Resistance | $R$ | $W$ |
| Electromotive force | $E$ | |
| Electrode potential, or discharge potential of an ion | $E$ | $\epsilon$ |
| Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero | $E_h$, $E_c$ | $\epsilon_h$, $\epsilon$ |
| Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration | ${}_0E_h$, ${}_0E_c$ | ${}_0\epsilon_h$, ${}_0\epsilon$ |
| Dielectric constant | $\epsilon$ | |
| Conductivity (specific conductance) | $\kappa$ | |
| Equivalent conductivity | $\Lambda$ | |
| Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent | $\Lambda_{10}$, $\Lambda_v$, $\Lambda_\infty$ | |

6. *Electricity and Magnetism*—(continued).

| | Usual symbol. | Alternative symbol. |
|---|---|---|
| Equivalent conductivity of kation and of anion | $\Lambda_k$, $\Lambda_a$ | |
| Equivalent conductivity of specified ions | $\Lambda_{K^+}$, $\Lambda_{Cl^-}$ | |
| Molecular conductivity | $\mu$ | |
| Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. | $U_k$, $U_a$ | |
| Transport number of kation and of anion | $n_k$, $n_a$ | |
| Magnetic permeability | $\mu$ | |
| Magnetic susceptibility | $\kappa$ | |

## *List of Symbols, Arranged Alphabetically.*

| Symbol. | Name of quantity. |
|---|---|
| $A$ | Atomic weight; maximum work. |
| $a$ | Van der Waals's constant. |
| $b$ | Van der Waals's constant. |
| $C$ | Concentration; molecular heat. |
| $c$ | Concentration; specific heat. |
| $C_p$, $C_v$ | Molecular heat at constant pressure, and at constant volume. |
| $c_p$, $c_v$ | Specific heat at constant pressure, and at constant volume. |
| $D$ | Alternative symbol for density. |
| $d$ | Diameter; total differential; density. |
| $d_c$ | Critical density. |
| $d_r$ | Reduced density. |
| $E$ | Electromotive force; electrode potential. |
| $e$ | Base of Napierian logarithms; charge on an electron. |
| $E_h$, $E_c$ | Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero. |
| ${}_0E_h$, ${}_0E_c$ | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration. |
| $F$ | Faraday's constant (number of coulombs per gram-equivalent of an ion). |
| $g$ | Acceleration due to gravity. |
| $h$ | Height. |
| $I$ | Current. |
| $i$ | Van't Hoff's coefficient. |
| $J$ | Mechanical equivalent of heat. |
| $K$ | Equilibrium constant. |
| $K_c$, $K_p$ | Equilibrium constant, when molar concentrations and partial pressures respectively are employed. |
| $k$ | Velocity coefficient of reaction. |
| $L$ | Latent heat per mole. |
| $l$ | Length; latent heat per gram. |
| $M$ | Molecular weight. |
| $M[\alpha]$ | Molecular rotatory power. |
| $M[\omega]$ | Molecular magnetic rotatory power. |
| $m$ | Mass. |
| $N$ | Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule. |
| $n$ | Refractive index. |

## *List of Symbols, Arranged Alphabetically*—(continued).

| Symbol. | Name of quantity. |
|---|---|
| $n_k$, $n_a$ | Transport number of kation and of anion. |
| $n_r$ | Refractive index (alternative symbol). |
| $P$ | Pressure. |
| $p$ | Pressure. |
| $p_c$, $p_r$ | Critical pressure : reduced pressure. |
| $Q$ | Quantity of heat; quantity of electricity. |
| $R$ | Gas constant per mole; electrical resistance. |
| $R_G$, $R_L$ | Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively. |
| $r$ | Radius. |
| $r_G$, $r_L$ | Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively. |
| $S$ | Entropy. |
| $T$ | Absolute temperature. |
| $T_c$ | Critical temperature (on the absolute scale). |
| $T_r$ | Reduced temperature (absolute). |
| $T_{cs}$ | Critical solution temperature (absolute). |
| $t$ | Time; temperature (centigrade). |
| $t_c$ | Critical temperature (centigrade). |
| $t_{cs}$ | Critical solution temperature (centigrade). |
| $t_r$ | Reduced temperature (centigrade). |
| $U_k$, $U_a$ | Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. |
| $V$ | Volume. |
| $v$ | Volume. |
| $v_c$, $v_r$ | Critical volume : reduced volume. |
| $W$ | Electrical resistance (alternative symbol). |
| $x$ | Mole fraction. |
| $\alpha$ | Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation. |
| $[\alpha]$ | Specific rotatory power. |
| $\gamma$ | Surface tension; ratio of specific heats. |
| $\Delta$ | Diffusion coefficient. |
| $\delta$ | Variation. |
| $\partial$ | Partial differential. |
| $\epsilon$ | Electrode potential (alternative symbol); dielectric constant. |
| $\epsilon_h$, $\epsilon$ | Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols). |
| ${}_0\epsilon_h$, ${}_0\epsilon_c$ | Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols). |
| $\eta$ | Viscosity. |
| $\theta$ | Temperature (centigrade), (alternative symbol). |
| $\kappa$ | Specific conductance (conductivity); magnetic susceptibility. |
| $\Lambda$ | Equivalent conductivity. |
| $\Lambda_{10}$, $\Lambda_v$, $\Lambda_\infty$ | Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent). |
| $\Lambda_k$, $\Lambda_a$ | Equivalent conductivity of kation and of anion. |
| $\lambda$ | Wave-length of light. |
| $\mu$ | Molecular conductivity; magnetic permeability. |
| $\pi$ | Ratio of circumference to diameter. |
| $\Sigma$ | Summation. |
| $\sigma$ | Surface tension (alternative symbol). |
| $\phi$ | Fluidity. |
| $[\omega]$ | Specific magnetic rotation. |

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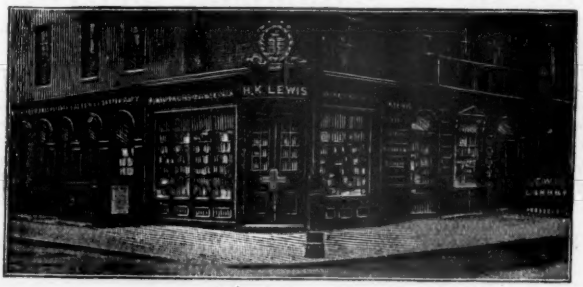


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## ERRATA.

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| Page | Line | |
|---|---|---|
| 1323 | 11 | *for* "4·9" *read* "4·0." |
| 1543 | 14 | *for* "tetralene" *read* "tetralin." |
| ,, | 15* | *for* "phenolphthalein" *read* "phenolphthalin." |
| 1934 | 6 | (and throughout the paper) *for* "diphenylsuccinalic" *read* "diphenylsuccinanilic." |
| 2377 | | Formula II, *for* "CHBr" *read* "$CH_2$." |
| ,, | 2 | *for* "Bromocampholenic" *read* "Campholenic." |

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